

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re the Patent Application of Marc SCHAEPKENS *et al.*

Confirmation No.: 7897

Application No.: 10/779,373 Art Unit: 1794

Filed: 17 February 2004 Examiner: Kevin R. Kruer

Title: COMPOSITE ARTICLES HAVING DIFFUSION BARRIERS AND  
DEVICES INCORPORATING THE SAME

**APPEAL BRIEF**

**Mail Stop: Appeal Brief-Patents**  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

Pursuant to 37 C.F.R. § 41.37, Applicants hereby submit this appeal brief. The appeal brief is being timely submitted under 37 C.F.R. § 41.37(a) and § 1.136, the mail date of the Notice of Panel Decision from Pre-Appeal Brief Review being May 12, 2009.

Respectfully Submitted,

/mcc/

Mark C. Comtois

Reg. No. 46,285

Duane Morris LLP  
505 9<sup>th</sup> Street, N.W., Suite 1000  
Washington, D.C. 20004-2166  
TEL: 202-776-7800  
FAX: 202-776-7801

**June 12, 2009**

## TABLE OF CONTENTS

I.	Real Party in Interest .....	1
II.	Related Appeals and Interferences .....	1
III.	Status of Claims.....	1
IV.	Status of Amendments.....	1
V.	Summary of Claimed Subject Matter .....	1
VI.	Grounds of Rejection To Be Reviewed on Appeal .....	3
	A. Whether Claims 1, 4, 6-8, 11, 13 and 14 are subject to rejection under 35 U.S.C. §103(a) as being unpatentable over Chung, et al. (U.S. Patent No. 6,836,070) in view of Otto, et al. (U.S. Patent No. 5,643,638).....	3
	B. Whether Claims 1, 4-8 and 11-14 are subject to rejection under 35 U.S.C. §103(a) as being unpatentable over Graff, et al. (U.S. Patent No. 6,492,026) in view of Otto, et al. .....	3
	C. Whether Claims 1, 4-5, 7, 8 and 11-15 are subject to rejection under 35 U.S.C. §103(a) as being unpatentable over Silvernail, et al. (U.S. Patent No. 6,576,351) in view of Otto, et al. ....	3
VII.	Argument .....	3
	A. The “varies...continuously” feature. ....	4
	B. Otto does not disclose the “varies...continuously” feature. ....	7
	C. The proposed combinations of Chung, Graff or Silvernail in view of Otto as presented by the Office fails to meet the “varies...continuously” feature. ....	9
	1. The Office acknowledges that Chung, Graff and Silvernail fail to disclose “varies... continuously” feature. ....	9
	2. The Office’s combination uses the method of Otto to make Chung’s/Graff’s/Silvernail’s alternating organic/barrier layers. ....	9
	3. Using the method taught in Otto to make the alternating organic/barrier layers of Chung, Graff and Silvernail results in the alternating organic/barrier layers of Chung, Graff and Silvernail....	9
VIII.	Conclusion .....	10
IX.	Claims Appendix .....	11
X.	Evidence Appendix.....	14
	A. Declaration Under 37 C.F.R. § 1.132 .....	14
XI.	Related Proceedings Appendix.....	39
	A. None.....	39

**I. Real Party in Interest**

The real party in interest is General Electric Company, present owner of the application and the invention described therein.

**II. Related Appeals and Interferences**

Appeal of U.S. Application No. 10/779,373 titled, "Composite Articles Having Diffusion Barriers and Devices Incorporating the Same." There are no related appeals or interferences.

**III. Status of Claims**

Claims 1, 4-8, and 11-15 are pending in the present application. Claims 1, 4-8, and 11-15 stand rejected, and their rejection is hereby appealed. Claims 16-26 are withdrawn from consideration.

**IV. Status of Amendments**

No amendments have been filed subsequent to the Final Office Action of December 10, 2008.

**V. Summary of Claimed Subject Matter**

Applicants' subject matter generally relates to composite films having improved resistance to diffusion of chemical species and to articles and apparatus incorporating such composite films. More specifically, the claimed subject matter is directed to composite articles having a first and second polymeric substrate layer where each of the polymeric substrate layers is coated with at least a diffusion-inhibiting barrier such that the diffusion-inhibiting barriers on the substrate layers face each other within the composite article, and where at least one of the

diffusion-inhibiting barriers includes a material having a composition that varies substantially continuously across a thickness thereof. The claimed subject matter is also directed in part to an apparatus including the composite article and an electronic device disposed on the composite article.

The composite article 10 comprising a first polymeric substrate layer 20 and a second polymeric substrate layer 24 as recited in Claim 1 is shown in Figure 1. (Figure 1, Specification page 6, ll. 13-17). Each of the polymeric substrate layers 20, 24 has at least a diffusion inhibiting barrier 30, 34 disposed on a surface thereof, wherein the diffusion-inhibiting barriers 30, 34 on the substrate layers 20, 24 face each other within the composite article 10. (Figure 1, Specification page 6, ll. 20-26). At least one of the diffusion inhibiting barriers 30, 34 comprises a material, the composition of which varies substantially continuously across a thickness thereof. (Figure 8, Specification as amended in Amendment filed June 4, 2007, now page 14, ¶ [0046] including Col. 6, ll. 62-66 of U.S. Patent No. 7,015,640 incorporated by reference in originally filed Specification; page 11, ll. 16-19; page 8, ll. 10-12; page 7, ll. 1-2). Compositions of the at least one diffusion-inhibiting barrier 30, 34 are selected from the group consisting of organic materials and inorganic materials. (Specification page 8, ll. 10-12; page 7, ll. 1-5).

The apparatus 100 comprises a composite article 10 that includes a first polymeric substrate layer 20 and a second polymeric substrate layer 24, each of the polymeric substrate layers 20, 24 having at least a diffusion-inhibiting barrier 30, 34 disposed on a surface thereof, wherein the diffusion-inhibiting barriers 30, 34 on the substrate layers 20, 24 face each other within the composite article 10; and an electronic device 110 disposed on the composite article

10, wherein at least one of the diffusion-inhibiting barriers 30, 34 comprises a material, the composition of which varies substantially continuously across a thickness thereof, and wherein compositions of regions across a thickness of the at least one diffusion-inhibiting barrier are selected from the group consisting of organic materials and inorganic materials as recited in Claim 8. See e.g., (Figures 1, 6, 8; Specification page 6, ll. 13-17; page 6, ll. 20-26; page 11, ll. 16-19; page 8, ll. 10-12; page 7, ll. 1-5; page 12, ll. 16-23; Specification as amended in Amendment filed June 4, 2007, now page 14, ¶ [0046] including Col. 6, ll. 62-66 of U.S. Patent No. 7,015,640 incorporated by reference in originally filed Specification).

## **VI. Grounds of Rejection To Be Reviewed on Appeal**

**A. Whether Claims 1, 4, 6-8, 11, 13 and 14 are subject to rejection under 35 U.S.C. §103(a) as being unpatentable over Chung, et al. (U.S. Patent No. 6,836,070) in view of Otto, et al. (U.S. Patent No. 5,643,638).**

**B. Whether Claims 1, 4-8 and 11-14 are subject to rejection under 35 U.S.C. §103(a) as being unpatentable over Graff, et al. (U.S. Patent No. 6,492,026) in view of Otto, et al.**

**C. Whether Claims 1, 4-5, 7, 8 and 11-15 are subject to rejection under 35 U.S.C. §103(a) as being unpatentable over Silvernail, et al. (U.S. Patent No. 6,576,351) in view of Otto, et al.**

## **VII. Argument**

Independent Claims 1 and 8 were improperly rejected as being unpatentable over Chung, Graff or Silvernail in view of Otto. The issues with respect to each of these prior art rejections are the same and are appropriately treated together. Independent Claims 1 and 8 recite, *inter alia*,

the following limitation: “*at least one of said diffusion-inhibiting barriers comprises a material, the composition of which varies substantially continuously across a thickness thereof*” (hereinafter the “varies...continuously” feature). All the arguments are related to this feature. The Applicant suggests that the prior art reference, Otto, does not disclose the “varies...continuously” feature as relied upon by the Office and further notwithstanding Otto’s teachings, the Office’s proposed combination as stated also does not meet the “varies...continuously” feature. As such, the Applicant submits the Office has failed to establish a *prima facie* case of obviousness as each and every limitation of the claims is not met. To establish *prima facie* obviousness of a claimed invention, all the claim limitations must be taught or suggested by the prior art. *In re Royka*, 490 F. 2d 981, 180 USPQ 580 (CCPA 1974).

#### A. The “varies...continuously” feature.

The term “continuously” in the “varies...continuously” feature is dispositive in this case.

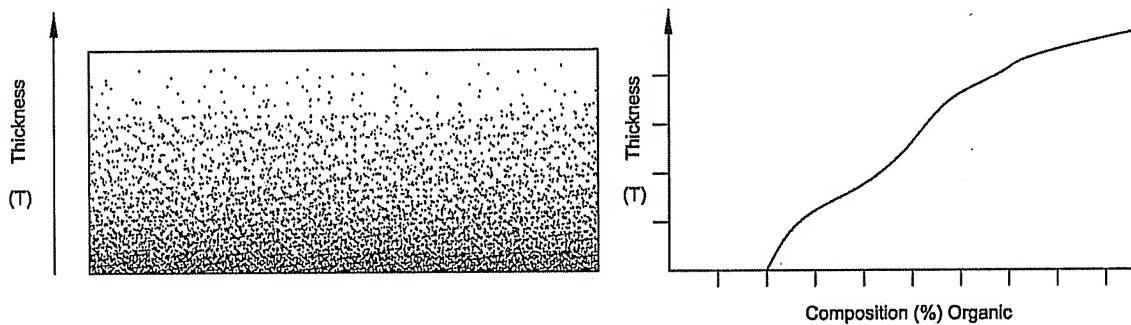
The American Heritage Dictionary defines “Continuous” as “of or relating to line or curve that extends without a break or irregularity”<sup>1</sup>. This is in contrast to the definition of “discontinuous”<sup>2</sup>.

---

1. “continuously,” in *The American Heritage® Dictionary of the English Language, Fourth Edition*. Source location: Houghton Mifflin Company, 2004. <http://dictionary.reference.com/browse/continuously>. Available: <http://dictionary.reference.com>. Accessed: June 09, 2009.

2. “discontinuously” *Id.*( “Possessing one or more discontinuities, as a function”)

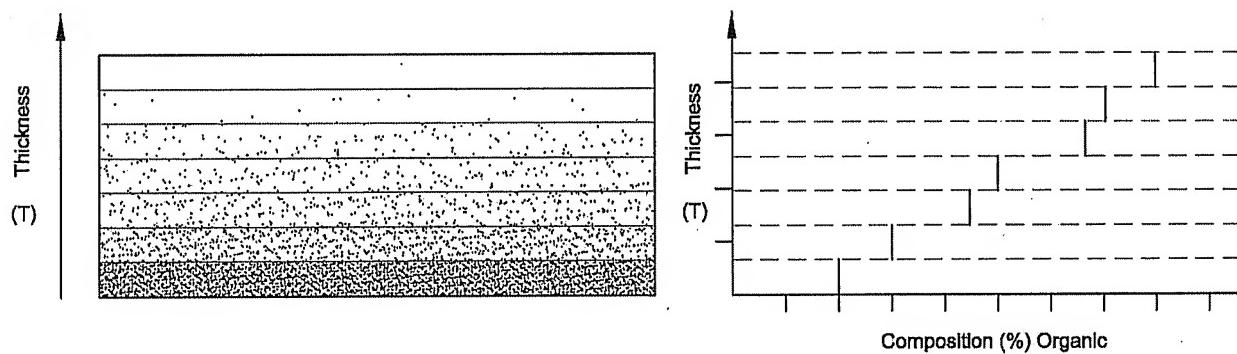
Figure 1, below, is an illustration depicting a representative barrier layer as described, *inter alia*, by the “varies...continuously” feature in the claims and a chart reflecting the respective variation in material composition through the thickness.



**Figure 1**

As shown in the above chart, the percentage of organic material in the layer increases substantially continuously across the thickness (T). ***There are no discontinuities, breaks or irregularities.*** In the illustration of the barrier layer, the inorganic material is represented by stippling. The amount of inorganic material decreases substantially continuously throughout the thickness. The transition between the dark (inorganic) bottom to the light (organic) top portion in the barrier layer is shown as substantially continuous.

In contrast, Figure 2, below is an illustration depicting a representative barrier layer comprised of individual sublayers that varies “discontinuously” and a chart reflecting the constant material composition in each sublayer.



**Figure 2**

As shown in the above chart, the percentage of organic material in the overall barrier layer increases in a discrete step wise function, from one sublayer to another sublayer. In each of the sublayers, the composition of organic material remains unchanged (each sublayer has uniform shading and the chart shows a vertical line (*i.e.*, constant composition) for each sublayer). At an interface between the sublayers, there is a jump or discontinuity in the composition as reflected in the chart on the right. Rather than a gradual substantially continuous change in composition, there is an abrupt break, an irregularity of the composition between sublayers.

**B. Otto does not disclose the “varies...continuously” feature.**

Otto discloses a plasma pulse CVD method. Otto states:

“By using the plasma pulse CVD method according to the invention, elementary layers (*single layers*) of different composition can be deposited. The elementary layers are deposited in a targeted manner pulse for pulse by appropriate selection of the pulse amplitude.” (see Otto, col. 3 ll. 27-31, emphasis added)

Otto, however, fails to disclose a plasma pulse CVD method that produces a barrier layer according to the limitation at issue. To the contrary, Otto discloses *producing a coating by depositing a single (“elementary”) layer for each power pulse.* “In these [plasma pulse CVD] methods, the electromagnetic radiation which excites the plasma is supplied in a pulsed manner. . . . *With each pulse, a thin layer . . . is deposited on the substrate.*” (see Otto, col. 2 ll. 49-53; emphasis added) Each of the individual layers *may* have a composition which is different than the composition of the layer on either side of it.

“For producing a gradient layer, one would, as a rule, proceed such that, in an initial experimental sequence, the dependence of the layer characteristics or layer compositions from pulse duration, pulse amplitude and pulse interval is determined. For producing the actual gradient layer, these parameters are so controlled that the desired gradient occurs in the direction of growth of the layer. *The precision with which the gradient is determined initially is governed by the requirements imposed on the layers. According*

*to the method of the invention, it is possible without difficulty to change the composition of the layer on the substrate in the direction of layer growth from one layer to the next.” (see Otto, col. 6 ll. 20-31; emphasis added)*

Otto produces a gradient layer from a plurality of layers, one at a time, similar to the discontinuous barrier layer illustrated in Figure 2 above.

Otto is limited to depositing one individual layer per power pulse which is homogenous in composition across its thickness, thereby creating a coating composed of multiple individual layers each having a different, constant composition. Creating a coating containing multiple individual layers where a gradient may be formed not within a particular layer but across multiple single layers that are stacked on top of each other is disparate from the claimed barrier having the “varies...continuously” feature.

The Office’s position that “Otto teaches the composition is adjusted “virtually without delay (col. 5, lines 43+)” (see Final Office Action dated 12/10/2008, page 6 second full paragraph) does not refute the fact that Otto’s method deposits single, individual layers. While Otto may be able to deposit the individual layers faster than the prior art (which is an object of the invention – see Otto, col. 2 ll. 35-37), Otto is limited to depositing one individual layer per power pulse, where each individual layer has a constant composition, thereby creating a coating composed of multiple individual layers. Again, this is disparate from the claimed barrier where “at least one of said diffusion-inhibiting barriers comprises a material, the composition of which varies substantially continuously across a thickness thereof.” Accordingly, it is respectfully requested that all the rejections for each of Claims 1 and 8 be withdrawn.

**C. The proposed combinations of Chung, Graff or Silvernail in view of Otto as presented by the Office fails to meet the “varies...continuously” feature.**

1. The Office acknowledges that Chung, Graff and Silvernail fail to disclose “varies... continuously” feature.

“Chung [Graff, Silvernail] does not teach that the composition of the organic and inorganic layers should vary substantially continuously across the thickness of the composite.”

(See Final Office Action mailed 12/10/08, pages 3-5.)

2. The Office’s combination uses the method of Otto to make Chung’s/Graff’s/Silvernail’s alternating organic/barrier layers.

The Office states:

“Thus it would have been obvious to the skilled artisan at the time the invention was made to utilize the method taught in Otto to make the alternating organic/barrier layers[alternating organic and inorganic layers] taught in Chung [Graff, Silvernail].” Final Office Action 12/10/08, pg. 3,4,5.

3. Using the method taught in Otto to make the alternating organic/barrier layers of Chung, Graff and Silvernail results in the alternating organic/barrier layers of Chung, Graff and Silvernail.

The Office’s use of Otto in making the alternating organic/barrier layers (organic and inorganic layers) results simply in the organic/barrier layers as described in Chung, Graff and Silvernail. As noted by the Office, the alternating organic/barrier layers of Chung, Graff and Silvernail do not have layers whose composition varies substantially continuously across the thickness of the composite. Therefore, using the method of Otto to make these layers does not

change the discontinuously varying characteristics of the layers, and the Office's combination does not provide the "varies...continuously" feature.

### VIII. Conclusion

The Applicant has demonstrated that the prior art reference Otto does not disclose the "varies...continuously" feature as relied upon by the Office. The Applicant has also demonstrated that irrespective of Otto's teachings, the Office's proposed combination does not meet the "varies...continuously" feature. The Office has thus failed to establish a *prima facie* case of obviousness as each and every limitation of the claims is not met. The Applicant request that the standing rejections be withdrawn and the application including Claims 1, 4-8 and 11-15 be allowed.

**IX. Claims Appendix**

1. A composite article comprising a first polymeric substrate layer and a second polymeric substrate layer, each of said polymeric substrate layers having at least a diffusion-inhibiting barrier disposed on a surface thereof, wherein the diffusion-inhibiting barriers on said substrate layers face each other within said composite article and at least one of said diffusion-inhibiting barriers comprises a material, the composition of which varies substantially continuously across a thickness thereof, and wherein compositions of regions across a thickness of said at least one diffusion-inhibiting barrier are selected from the group consisting of organic materials and inorganic materials.

2. (Canceled)

3. (Canceled)

4. The composite article according to claim 1, wherein at least one diffusion-inhibiting barrier comprises a plurality of alternating sublayers of at least an organic polymeric material and at least an inorganic material.

5. The composite article according to claim 4; wherein said inorganic material is selected from the group consisting of metals, metal oxides, metal nitrides, metal carbides, metal oxynitrides, metal oxyborides, and combinations thereof; and said organic material is selected from the group consisting of polyacrylates, polyurethanes, polyamides, polyimides, polybutylenes, isobutylene isoprene, polyolefins, epoxies, parylene, benzocyclobutadiene,

polynorbornenes, polyarylethers, polycarbonate, alkyds, polyaniline, ethylene vinyl acetate, ethylene acrylic acid, derivatives thereof, and combinations thereof.

6. The composite article according to claim 1, further comprising a chemically resistant hardcoat disposed on a surface of one of said polymeric substrate layers opposite to a diffusion-inhibiting barrier.

7. The composite article according to claim 1, further comprising a layer of an electrically conducting material disposed on a surface of one of said polymeric substrate layers opposite to a diffusion-inhibiting barrier.

8. An apparatus comprising:

(a) a composite article that comprises a first polymeric substrate layer and a second polymeric substrate layer, each of said polymeric substrate layers having at least a diffusion-inhibiting barrier disposed on a surface thereof, wherein the diffusion-inhibiting barriers on said substrate layers face each other within said composite article; and

(b) an electronic device disposed on said composite article, wherein at least one of said diffusion-inhibiting barriers comprises a material, the composition of which varies substantially continuously across a thickness thereof, and wherein compositions of regions across a thickness of said at least one diffusion-inhibiting barrier are selected from the group consisting of organic materials and inorganic materials.

9. (Canceled)

10. (Canceled)

11. The apparatus according to claim 8, wherein at least one diffusion-inhibiting barrier comprises a plurality of alternating sublayers of at least an organic polymeric material and at least an inorganic material.

12. The apparatus according to claim 11, wherein said inorganic material is selected from the group consisting of metals, metal oxides, metal nitrides, metal carbides, metal oxynitrides, metal oxyborides, and combinations thereof; and said organic material is selected from the group consisting of polyacrylates, polyurethanes, polyamides, polyimides, polybutylenes, isobutylene isoprene, polyolefins, epoxies, parylene, benzocyclobutadiene, polynorbornenes, polyarylethers, polycarbonate, alkyds, polyaniline, ethylene vinyl acetate, ethylene acrylic acid, and combinations thereof.

13. The apparatus according to claim 8, wherein said electronic device comprises an electronically active material disposed between a pair of electrodes.

14. The apparatus according to claim 13, wherein said electronic device is an organic electroluminescent device.

15. The apparatus according to claim 13, wherein said electronic device is an organic photovoltaic device.

16-26. (Withdrawn)

**X. Evidence Appendix.****A. Declaration Under 37 C.F.R. § 1.132**

The Applicant submitted a Declaration under 37 C.F.R. § 1.132 of Min (Martin)Yan with the Applicant's Amendment and Request for Continued Examination on June 4, 2007 (Min Yan is an employee of assignee). The Applicant also submitted the following two non-patent literature documents concurrently with the Declaration:

(a) Min Yan, Tae Won Kim, Ahmet Gün Erlat, Matthew Pellow, Donald F. Foust, Jie Liu, Marc Schaepkens, Christian M. Heller, Paul A. McConnelee, Thomas P. Feist, and Anil R. Duggal, "A Transparent, High Barrier, and High Heat Substrate for Organic Electronics", Proceedings of The IEEE, 93 (8), 1468-1477 (2005).

(b) Tae Won Kim, Min Yan, Ahmet Gün Erlat, Paul A. McConnelee, Mathew Pellow, John Deluca, Thomas P. Feist, and Anil R. Duggal, "Transparent Hybrid Inorganic/Organic Barrier Coatings for Plastic Organic Light-emitting Diode Substrates", Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 23:(4), 971-977 (2005).

The Office stated that it entered Applicant's submission on page 2 of the Office Action mailed May 23, 2008.

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re the Patent Application of : Marc SCHAEPKENS, et al.

Serial No.: 10/779,373

Art Unit: 1773

Filed: 17 February 2004

Examiner: Kevin R. Kruer

Title: COMPOSITE ARTICLE HAVING DIFFUSION BARRIERS AND DEVICES INCORPORATING THE SAME

**DECLARATION UNDER 37 CFR § 1.132**

I, Min (Martin) Yan, hereby declare as follows:

1. I have a Ph.D. degree in Materials Science and Engineering from Northwestern University in Evanston, Illinois, U.S.A., a M.S. degree in Materials Science from Shanghai Jiao Tong University in Shanghai, PRC and a B.S. degree in Materials Science from Shanghai Jiao Tong University in Shanghai, PRC. During my academic career, I concentrated my studies on vacuum coatings and thin film growth. I have been working in the field of barrier layers, including diffusion-inhibiting barrier layers for more than five years. Particularly, I have been working with diffusion-inhibiting barrier layers having a composition which varies substantially continuously across a thickness of the layer and have published a number of papers on that subject (copies of which are attached) including the following:

(a) Min Yan, Tae Won Kim, Ahmet Gün Erlat, Matthew Pellow, Donald F. Foust, Jie Liu, Marc, Schaepkens, Christian M. Heller, Paul A. McConnelee, Thomas P.

Feist, And Anil R. Duggal, "A Transparent, High Barrier, and High Heat Substrate for Organic Electronics", Proceedings of The IEEE, 93 (8), 1468-1477 (2005).

(b) Tae Won Kim, Min Yan, Ahmet Gün Erlat, Paul A. McConnelee, Mathew Pellow, John Deluca, Thomas P. Feist, and Anil R. Duggal, "Transparent hybrid inorganic/organic barrier coatings for plastic organic light-emitting diode substrates", Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, 23:(4), 971-977 (2005).

I am intimately familiar with diffusion-inhibiting barrier layers and thoroughly knowledgeable with the meaning of the terminology "varying substantially continuously across a thickness" as it applies to diffusion-inhibiting barrier layers.

2. I understand that independent Claim 1 of the instant application currently reads as follows:

1. A composite article comprising a first polymeric substrate layer and a second polymeric substrate layer, each of said polymeric substrate layers having at least a diffusion-inhibiting barrier disposed on a surface thereof, wherein the diffusion-inhibiting barriers on said substrate layers face each other within said composite article and **at least one of said diffusion-inhibiting barriers comprises a material, the composition of which varies substantially continuously across a thickness thereof**, and wherein compositions of regions across a thickness of said at least one diffusion-inhibiting barrier are selected from the group consisting of organic materials and inorganic materials.  
(emphasis added)

3. I further understand that independent Claim 8 of the instant application currently reads as follows:

8. An apparatus comprising:
    - (a) a composite article that comprises a first polymeric substrate layer and a second polymeric substrate layer, each of said polymeric substrate layers having at least a diffusion-inhibiting barrier disposed on a surface thereof, wherein the diffusion-inhibiting barriers on said substrate layers face each other within said composite article; and
    - (b) an electronic device disposed on said composite article, wherein **at least one of said diffusion-inhibiting barriers comprises a material, the composition of which varies substantially continuously across a thickness thereof**, and wherein compositions of regions across a thickness of said at least one diffusion-inhibiting barrier are selected from the group consisting of organic materials and inorganic materials.
- (emphasis added)

Each of the two independent claims includes the limitation “at least one of said diffusion-inhibiting barriers comprises a material, the composition of which varies substantially continuously across a thickness thereof”.

4. Additionally, I understand that each of the two independent claims stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Chung, et al. (U.S. Patent No. 6,836,070, hereinafter “Chung”) in view of Moser (U.S. Patent Application Pub. No. US2003/0148139, hereinafter “Moser”) and Chopra (U.S. Patent No. 6,413,858, hereinafter “Chopra”). Additionally, Claims 1, 4-8, and 11-14 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Graff, et al. (U.S. Patent No. 6,492,026, hereinafter “Graff”) in view of Moser and Chopra. Furthermore, the two independent claims stand rejected under 35 U.S.C. § 103(a) as unpatentable over Silvernail (U.S. Patent No. 6,576,351, hereinafter “Silvernail”) in view of Moser and Chopra. The examiner groups the rejections into three groups based on the three primary references

(Chung, Graff, and Silvernail). Each of the three groups relies on secondary references Moser and Chopra to support the obviousness rejection: Moser for (a) the limitation of **an organic polymer layer varying substantially continuously across a thickness of the diffusion barrier** (“Limitation A”), or Chopra for (b) the limitation of an **inorganic layer varying substantially continuously across a thickness of the diffusion barrier** (“Limitation B”).

5. Regarding the diffusion barrier layer in Moser, the examiner relies on Moser to show a continuously varying organic polymer layer (Limitation A). Moser requires “metal-containing particles . . . formed as individual grains or as a conglomerate of several grains” (*see* Moser at [0011]) (emphasis added) where the metal-containing particles are dispersed in an organic layer matrix. Moser also discloses, at [0016], that “the concentration of metal-containing components decreases as the thickness of the protection and/or diffusion barrier layer increases, in particular the metal particles diminish continuously in the direction of the surface” in order to affect the electrical conductivity of the barrier layer. In other words, Moser teaches a suspension of metal particles in an organic layer matrix that allows the designer to tailor the electrical properties of the layer. While there appears to be a gradient of discrete particles in the Moser diffusion layer, this is not a layer where the composition of the layer varies substantially continuously across a thickness of the layer, as is that term is known in the art. Indeed, there is no disclosure anywhere in Moser that indicates that the organic layer varies substantially continuously across a thickness of the layer. Rather, it is a “matrix” the composition of which is constant throughout the thickness of the layer. Instead,

Moser's diffusion layer is like a suspension. Moser teaches step-wise discontinuities of metal particles in an organic layer matrix that is constant throughout the thickness of the diffusion layer.

6. The present application discloses and claims a diffusion-inhibiting barrier layer where the composition of the layer varies substantially continuously across a thickness of the layer.

(a) The Example on page 11 (paragraph [0035]) of the application discloses an embodiment of a layer with a continuously-varying composition across a thickness: "a graded (inorganic/organic) barrier coating with a composition that was initially inorganic in nature, then continuously changed into a dominantly organic nature, and finally changed back to an inorganic nature."

(b) Paragraph [0028] discloses another embodiment which illustrates a layer with a continuously-varying composition across a thickness: "In one embodiment, a graded composition of the coating is obtained by changing the compositions of the reactants fed into the reactor chamber during the deposition of reaction products to form the coating. Varying the relative supply rates or changing the identities of the reacting species results in a diffusion-inhibiting barrier or coating that has a graded composition across its thickness."

(c) Figure 4 of U.S. Patent No. 7,015,640 issued to Schaepkens, et al. (U.S. Application No. 10/065,018), which is incorporated by reference in the instant application, shows a further example of a diffusion-inhibiting layer having a composition which varies substantially continuously across a thickness of the layer. As described in

the Schaepkens patent at col. 6 lines 62-66, Figure 4 shows the composition of the coating as a function of sputtering time which is related directly to the depth of the coating. As can be seen from Figure 4, the composition of the components of carbon, silicon, and nitrogen vary across the thickness of the coating.

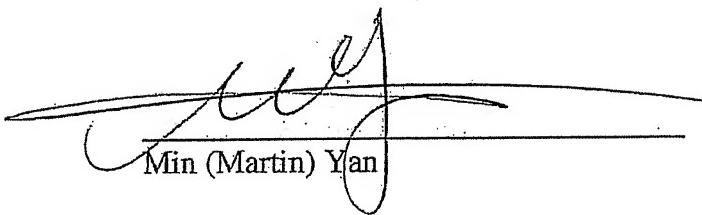
The embodiments described in 6(a), 6(b), and 6(c) are examples of the meaning in the art of the terminology of a diffusion-inhibiting barrier comprising a material, the composition of which varies substantially continuously across a thickness thereof.

7. Therefore, the diffusion barrier layer in Moser is not a layer for which the composition varies substantially continuously across a thickness of the layer, as that term is understood in the art.

8. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Title 18, United States Code, Section 1001, and that such willful false statements may jeopardize the validity of the above-identified application or any patent issuing thereon.

Respectfully submitted,

DATE: 06/04/2007



Min (Martin) Yan

# A Transparent, High Barrier, and High Heat Substrate for Organic Electronics

MIN YAN, TAE WON KIM, AHMET GÜN ERLAT, MATTHEW PELLOW, DONALD F. FOUST, JIE LIU, MARC SCHAEPKENS, CHRISTIAN M. HELLER, PAUL A. McCONNELEE, THOMAS P. FEIST, AND ANIL R. DUGGAL

*Invited Paper*

*The use of plastic film substrates for organic electronic devices promises to enable new applications, such as flexible displays and conformal lighting, and a new low-cost paradigm through high-volume roll-to-roll fabrication. Unfortunately, presently available substrates cannot yet deliver this promise because of the challenge in achieving the required combination of optical transparency, impermeability to water and oxygen, mechanical flexibility, high-temperature capability, and chemical resistance. Here, we describe the development and performance of a plastic substrate comprising a high heat polycarbonate film combined with a unique transparent coating package that is aimed at meeting this challenge.*

**Keywords**—Flexible display, organic light-emitting devices (OLEDs), permeation barrier, plastic substrate.

## I. INTRODUCTION

The promise of organic electronics lies in the potential for building large area electronic devices with much lower cost than possible with conventional silicon-based technology [1]. The main reason for this is that the active layers of the device can be applied using low cost printing techniques that are compatible with high-volume “roll-to-roll” manufacturing. Example low-cost electronic technologies that have been demonstrated include organic light-emitting devices (OLEDs) [2], [3], organic photovoltaic devices [4]–[6], thin-film transistors (TFTs) and TFT arrays using

both organic [7]–[9] and solution-processible inorganic materials [10], [11], and more complicated circuits [12]–[14]. OLEDs represent the most advanced of these technologies as evidenced by the fact that OLED display products are now commercially available. However, these products are still manufactured using predominantly batch-mode conventional semiconductor fabrication processes and so have still not demonstrated the low cost and large area potential of organic electronics. Thus, considerable research effort is being directed toward fabricating OLEDs using printing processes on roll-to-roll compatible, mechanically flexible substrates. A key impediment for this effort is the lack of availability of a mechanically flexible substrate that fulfills all the requirements for a functional OLED. In this paper, we describe progress toward developing such a substrate.

The key requirements for a roll-to-roll compatible plastic OLED substrate are optical transparency, mechanical flexibility, chemical resistance, thermal stability, and impermeability to OLED degradation accelerants such as water and oxygen. Optical transparency is required for the most common “down-emitting” device structure where the transparent electrode is the first device layer deposited onto the substrate. Typical display applications require that the substrate exhibit >90% transmittance over the 400–700 nm visible range. It should be noted that optical transparency is not necessarily required in a substrate used for “up-emitting” OLED architectures, but these approaches face other design constraint and manufacturing integration issues.

Mechanical flexibility is required for roll-to-roll processing and for various envisioned end-use applications such as “roll-up” displays. A typical metric to quantify this is the ability to bend over a 1-in diameter 1000 times. Chemical resistance is required for substrate compatibility with the solvents and chemicals used in organic electronic device fabrication steps. A typical list of the materials that the substrate must be compatible with includes methanol,

Manuscript received October 28, 2004; revised February 14, 2005. This work was supported in part by the U.S. Display Consortium/Applied Research Laboratory (USDC/ARL) program MDA972-93-2-0014 and in part by the National Institute of Standards and Technology (NIST) ATP program 70NANB3H3030.

The authors are with General Electric Global Research Center, Niskayuna, NY 12309 USA (e-mail: yanm@crd.ge.com; kmt@crd.ge.com; erlat@crd.ge.com; pellow@research.ge.com; foust@crd.ge.com; liuji@crd.ge.com; marc.schaepkens@gesm.ge.com; heller@crd.ge.com; mcconnelee@crd.ge.com; feist@research.ge.com; duggal@crd.ge.com).

Digital Object Identifier 10.1109/JPROC.2005.851483

isopropanol, acetone, tetrahydrofuran, n-*t*-ethylpyrrolidone, ethylacetate, sulfuric acid, glacial acetic acid, hydrogen peroxide, and sodium hydroxide.

Many plastic films can deliver the required combination of transparency, mechanical flexibility, and chemical resistance. However, the additional requirement for temperature stability then limits the choice of plastic film material. High-temperature-stability films are desired mainly for compatibility with high-temperature process steps. Such steps can range from simple drying steps where higher temperature results in faster processing to TFT material deposition where higher temperature results in higher performance. Specific processes have different temperature requirements and/or tradeoffs with temperature. Thus, there is not a consensus among the technical community around a single temperature value requirement for a substrate. However, a useful upper-limit target value is 350 °C as this is currently a lower-limit processing temperature for conventional high-performance  $\alpha$ -Si TFTs. At present, no transparent plastic film exists with this level of temperature stability but clearly, as new films are developed which come closer to meeting this goal, more high-performance organic electronic devices and/or applications become possible.

Impermeability to water and oxygen represents the most demanding technical requirement for a roll-to-roll compatible OLED substrate because the active organic materials and electrodes of an OLED degrade in the presence of water and oxygen [15]. Simple calculations suggest that in order to achieve a device lifetime of tens of thousand hours, the substrate must provide a barrier that limits diffusion to less than  $10^{-6}$  g/m<sup>2</sup>/day and  $10^{-5}$  cc/m<sup>2</sup>/day for water and oxygen, respectively [16]. This level of hermeticity is beyond the capability of any known plastic film as typical moisture diffusion rates of such materials are in the 1–100 g/m<sup>2</sup>/day range. For this reason, any plastic film based substrate for use with OLEDs will need to be coupled with some sort of transparent “ultra-high barrier” (UHB) coating to provide the required hermeticity. To date, the most promising mechanically flexible substrate solution that has been proposed consists of a polyethylene terephthalate (PET) film combined with a multilayer UHB coating [17], [18]. The multilayer consists of alternating inorganic and organic layers that collectively are transparent and thin enough to maintain adequate flexibility. Barrier performance in the range of  $10^{-6}$  g/m<sup>2</sup>/day [19] has been demonstrated and attributed to a mechanism whereby the organic layers decouple pinhole defects in the otherwise-impermeable inorganic layers such that water and oxygen are forced to follow a highly tortuous—and hence slow—diffusion path [20]. OLEDs with reasonable lifetime have recently been demonstrated with this substrate [21].

In spite of the promising performance of the PET substrate, there is still a long way to go in terms of achieving higher temperature stability since, depending on process details, PET is typically limited to 110 °C. In addition, the multilayer nature of the UHB may be susceptible to delamination with repeated mechanical or thermal cycling. Here, we describe an alternative approach to a substrate suitable for OLED processing that addresses some of these

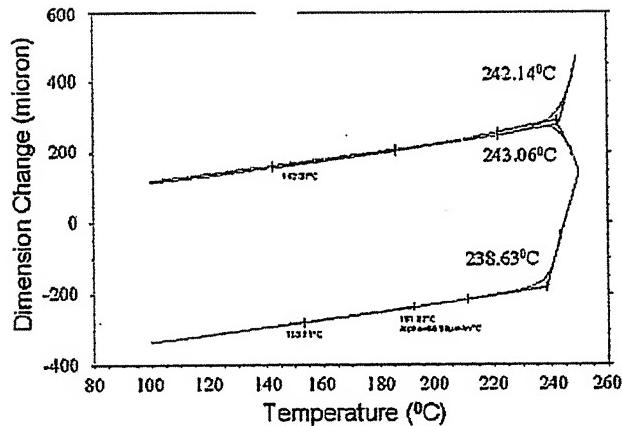


Fig. 1. Thermomechanical analysis performed on uncoated novel high heat polycarbonate film substrate. The temperatures at which one sees dramatic changes in dimensional change rate is a measure for the glass transition temperature.

limitations. The substrate is based on a high-temperature polycarbonate film coupled with a graded rather than a multilayer UHB coating. In this paper, we describe these two components of the substrate individually in the following two sections and then the performance of the combined package in Section IV.

## II. HIGH HEAT POLYCARBONATE SUBSTRATE

Commercially available Bisphenol A (BPA) polycarbonate, such as GE’s Lexan polycarbonate resin has a glass transition temperature ( $T_g$ ) around 150 °C. Higher  $T_g$  variants can be made by modifying the monomer. The novel polycarbonate material used in this work has a  $T_g$  around 240 °C, as determined by thermomechanical analysis (TMA); see Fig. 1. This novel polycarbonate material has significant advantages for developing high-temperature flexible substrates over other polymeric materials. These advantages include high-temperature process compatibility, high dimensional stability, high optical transparency, smooth surface, and low optical anisotropy. Films with a thickness of 125  $\mu$ m were made using this material through a solvent-casting process. Thermal and dimensional stability are critical to flexible organic device fabrication as these properties enable the substrate film to withstand the high-temperature deposition processes required for many device fabrication steps. As received, this polycarbonate film exhibits a shrinkage rate of 700–800 ppm/hr at 200 °C, which is too high for most optoelectronic device fabrication. However, its dimensional stability can be dramatically enhanced by a heat stabilization process. With exposure to a temperature slightly higher than its  $T_g$  for a short period of time, the shrinkage rate of this polycarbonate film is reduced to only 25 ppm/hr at 200 °C. The optical clarity of this polycarbonate substrate film is also excellent. Fig. 2 shows that this film is color neutral and has an average light transmittance of 90% in the visible light range.

A wide range of solvents and chemicals can potentially be used during flexible organic device fabrication. One limitation of polycarbonate materials in general is that they exhibit

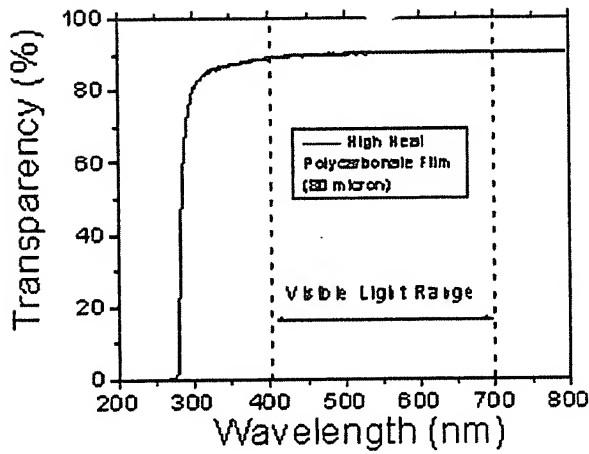


Fig. 2. Transmittance spectrum of uncoated novel high heat polycarbonate film substrate. The average transmittance of this high heat polycarbonate film in visible light range is 90.0%.



Fig. 3. Photographs of a chemical resistance layer coated (left) and uncoated (right) polycarbonate film after exposure for 10 min to acetone. No degradation is observed on the coated substrate.

poor solvent resistance and typically degrade in the presence of common processing chemicals. In order to overcome this, we developed an epoxy-based chemical resistance coating and applied it to both sides of the polycarbonate film. Fig. 3 shows a comparison between a coated and uncoated film when exposed to acetone. One can see that the optical quality of the polycarbonate film is degraded without the coating but effectively protected with the coating. In order to assess this strategy for providing chemical resistance, similar tests were performed with a full range of solvents typically used during organic electronic device fabrication and it was found that the epoxy-based coating protected the polycarbonate in all cases. Another potential issue with polycarbonate relates to dimensional instability due to water uptake since polycarbonate is known to absorb about 0.4% moisture at equilibrium [22]. However, with proper drying procedures, we were able to avoid any detrimental moisture uptake effects during our coating and device fabrication processes. Surface smoothness is another important base film feature because surface roughness can create defects in barrier coatings and electrical shorts in the active OLED. This polycarbonate film has nice surface properties as its average roughness is less than 1 nm and its peak-to-valley roughness is less than 20 nm. Hence, high heat polycarbonate coated with an epoxy-based chemical resistance layer was chosen as the base film for substrate development.

### III. UHB COATING

A great amount of literature has been accumulated during the past 20 years on applying vacuum deposited inorganic layers on polymer substrates in order to improve the barrier properties against water vapor and oxygen permeation [23]–[27]. Although bulk inorganics such as a perfect  $\text{SiO}_2$  film are effectively impermeable to moisture and oxygen [28], [29], single-layer inorganic barrier coatings only reduce the moisture and oxygen permeation rates by at most two to three orders of magnitude as compared to that through uncoated polymer [20], [25], [26], [30], [31]. The reason for the limited barrier improvement attainable with a single inorganic barrier coating is now well understood to be due to nanometer- to micrometer-size defects in the coating that originate either from the surface roughness of the underlying substrate or from the inorganic coating processing conditions [32]. These defects provide easy pathways for moisture and oxygen diffusion, and thus limit the barrier performance. Evidence of this defect-driven permeation mechanism can be found through studies of permeation rate as a function of inorganic coating thickness. Permeation rate through a defect-free bulk film should exhibit Fickian diffusion and should thus vary inversely with film thickness. However, this is not normally observed for thin-film barrier coatings. Typically, gas permeation rate reduces rapidly by two to three orders of magnitude with increasing coating thickness up to a “critical thickness” of 10–30 nm but, for larger thicknesses, the permeation rate does not decrease further [26]. Thus, regardless of barrier material or deposition method, the best barrier performance achieved so far from a single-layer inorganic coating is several orders of magnitude short of the OLED requirement.

In order to meet the stringent requirements put forth for the design of OLEDs and other organic electronic devices on plastic substrates, a robust coating design should be realized that avoids easy defect pathways for permeation. Multilayer barrier structures comprised of multiple sputter-deposited aluminum oxide inorganic layers separated by polymer multilayer (PML) processed organic layers have demonstrated promising moisture permeation rates in the range of  $10^{-6}$ – $10^{-5}$  g/m<sup>2</sup>/day [19], [33], [34]. It is commonly understood that organic layers decouple the defects in the inorganic layers and, thus, prevent the propagation of the defects from one inorganic layer to the other inorganic layers [35]. In other words, the multilayer stack stops defects from propagating in the vertical direction through the coating thickness. A modeling study suggests that this defect decoupling forces a tortuous path for moisture and oxygen diffusion, and thus reduces the permeation rate by several orders of magnitude [20]. Another study suggests that the inorganic–organic multilayer stack leads to higher performance through a transient rather than steady-state phenomenon [36]. Regardless of mechanism, this multilayer barrier stack approach appears to be capable of yielding the required level of performance for OLED applications.

One potential limitation of the multilayer stack approach is that this type of structure tends to suffer from poor adhesion

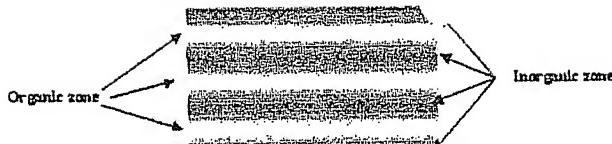


Fig. 4. Schematic of graded inorganic–organic UHB coating.

and delamination, especially during the thermal cycles of the OLED fabrication processes since the inorganic and organic layers have sharp interfaces with weak bonding structure due to the nature of the sputter deposition and PML processes [37], [38]. In order to overcome this, we have developed an alternative graded UHB coating that can effectively stop defects from propagating through the coating thickness. Furthermore, this graded UHB coating is less than 1  $\mu\text{m}$  thick, which is much thinner than that of a typical multilayer barrier stack. According to a simple calculation [39], this reduction in thickness can significantly reduce the effective edge diffusion of water through the organic portion of the barrier coating to be well below  $10^{-6} \text{ g/m}^2/\text{day}$ . The coating is fabricated using plasma enhanced chemical vapor deposition (PECVD) with a parallel plate capacitively coupled plasma reactor [39]. It consists of a novel, graded single layer made up of inorganic and organic materials as schematically shown in Fig. 4. In this barrier structure, the organic materials effectively decouple defects growing in the thickness direction but, instead of having a sharp interface between inorganic and organic materials, there are “transitional” zones where the coating composition varies continuously from inorganic to organic and vice versa. These “transitional” zones bridge inorganic and organic materials which should result in a single-layer structure with improved mechanical stability and stress relaxation [35], relative to that of multilayer barrier structures.

#### A. Graded UHB Process Development

There are two base PECVD processes required to fabricate the UHB coating—an inorganic and an organic process. The inorganic process utilizes a combination of silane, ammonia, and oxygen gases to create a material composition ranging between silicon nitride and silicon oxide. The organic process includes a combination of Si-containing organic precursor and Ar gases to create a Si-containing organic material. The inorganic and the organic processes were tailored such that the resulting materials have hardness (inorganic material: 10–15 GPa, organic material: <1 GPa) and elastic modulus (inorganic material: 50–100 GPa, organic material: <10 GPa) similar to those of glass-like materials and thermoplastics, respectively.

A PECVD inorganic film deposited on top of an organic material by nature has  $\sim 10 \text{ nm}$  of a “transitional” region that exhibits a continuously graded composition between the inorganic and organic material due to ion bombardment [35]. However, the high-energy ion bombardment normally results in a highly stressed film that adversely affects the adhesion of subsequent layers. For instance, an OLED device typically requires the deposition of a transparent conductive

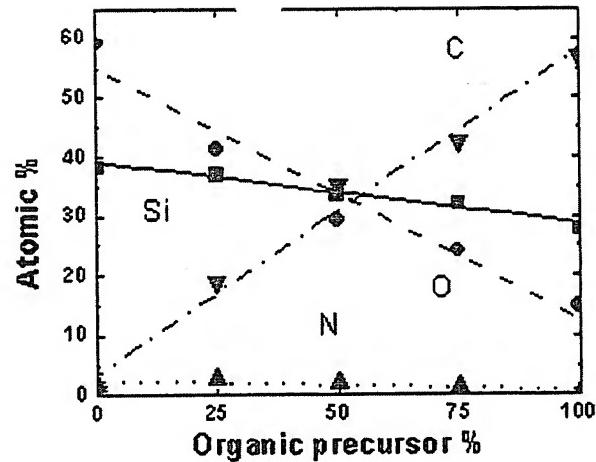


Fig. 5. X-ray photoelectron spectroscopy (XPS) analysis on the coating composition as a function of precursor gas composition.

oxide electrode such as indium–tin–oxide (ITO) on top of the UHB. A low-stress barrier coating is desirable for better adhesion of this layer. Thus, instead of resorting to high-ion bombardment energy, our graded UHB structure is obtained by gradually mixing the inorganic and the organic processes. At constant pressure and radio-frequency (RF) power, each mass flow controller (MFC) for each individual process gas is programmed to achieve continuous compositional changes, while the plasma remains on, in order to achieve a gradual change in the coating composition from inorganic to organic materials and vice versa. For example, if one wants to achieve a coating composition that comprises 90% of inorganic and 10% of organic materials, MFC values for the inorganic and the organic process gases are set at 90% and 10% with respect to their original values, respectively. The thickness of the “transitional” zone is determined by the time to change the precursor gas composition from the inorganic process to the organic process and vice versa. Typically due to the nonlinearity of the plasma process, mixing of precursors for two different processes often results in unexpected coating compositions unless the process conditions are carefully selected. In order to avoid such unexpected compositions, the inorganic and the organic processes were developed at the same pressure and RF power. In addition, the inorganic and the organic processes were engineered to have comparable deposition rates.

In order to ensure that coatings with mixed organic and inorganic compositions could be fabricated by keeping all PECVD process variables constant and only changing precursor gas composition, coatings were made and then analyzed for selected precursor gas combinations. Fig. 5 shows the results of X-ray photoelectron spectroscopy (XPS) analysis of these coatings. For these measurements, the coatings were deposited onto a silicon substrate and a few monolayers of the coating were removed from the top surface by low energy Ar sputtering to eliminate surface contamination effects. Fig. 5 indicates that a linear change in the coating composition can be achieved with a linear change in the precursor gas composition. For example, the carbon concentration is nearly zero when the precursor gas composition is that of the

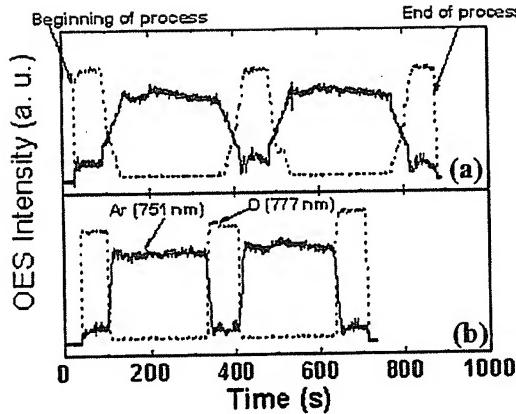


Fig. 6. Time-resolved optical emission spectra for PECVD graded UHB processes with (a) 40 nm and (b) 5 nm of “transitional” zone thickness.

pure inorganic process, and increases linearly with increasing percentage of the organic precursor. Note that the precursor gases for the organic process do not contain oxygen—the oxygen present in the 100% organic process is due to the background from the reactor.

Based on these results, processes were developed to create a single coating with the graded structure depicted in Fig. 4 and varying thickness “transition zones” between inorganic and organic compositions.

Fig. 6(a) and (b) compares the time-resolved optical emission spectra obtained during processing for two different processes with planned transition zones of 40 and 5 nm, respectively. For these measurements, representative emission lines (O at 777 nm for the inorganic process and Ar at 751 nm for the organic process) were selected to monitor the precursor composition change during the UHB deposition. The plasma was on for the whole time at constant pressure and RF power during the UHB process. Fig. 6 clearly indicates that a continuous change in the precursor composition is achieved during both UHB processes. The O emission intensity at 777 nm is high during the inorganic process, and decreases continuously toward a baseline when the fraction of the organic process gases monotonically increases during the “transitional” zone process. At the same time, Ar emission intensity increases continuously.

In order to verify that the desired graded composition coatings were made, depth-profile XPS measurements and cross-sectional transmission electron microscopy (TEM) were performed on the final coatings. The depth profile XPS analysis for the 40-nm transition zone sample shown in Fig. 6(a) is shown in Fig. 7. The data clearly suggests a continuous change in composition as a function of sputter time and hence depth. The XPS depth profiling was accomplished with low energy Ar sputtering. However, there is still the possibility that the apparently continuous change in composition observed may be an artifact caused by chemical changes of the surface induced by mixing or preferential sputtering of the elements [38]. In order to eliminate this interpretation, cross-sectional TEM analysis was performed in parallel on the same coating. Fig. 8 shows representative

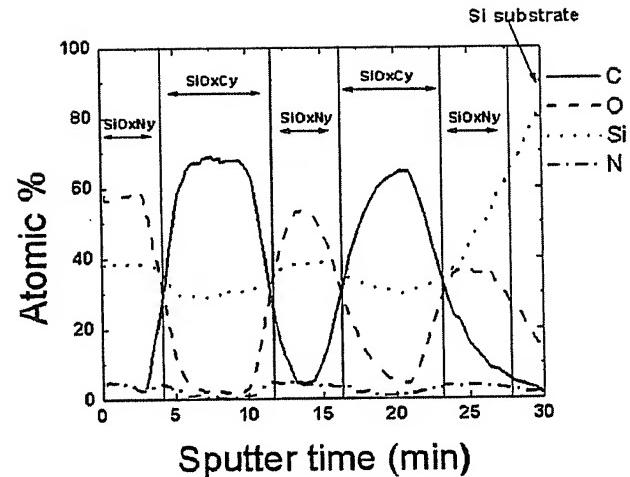


Fig. 7. XPS spectrum for graded inorganic–organic UHB coating.

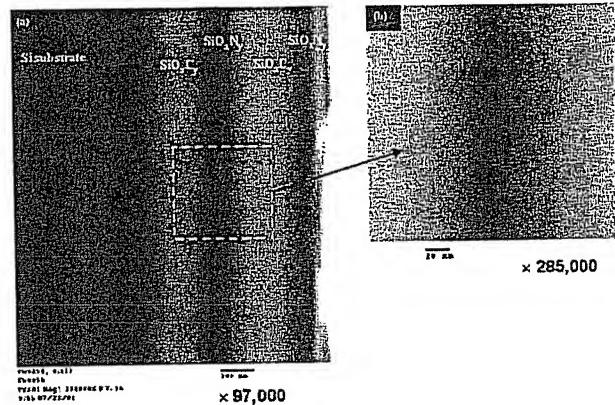


Fig. 8. Cross-section TEM images of graded UHB coating. (a) Low magnification. (b) High magnification.

TEM images. The images clearly show that the coating has a graded structure without a discrete interface.

#### B. Refractive Index Optimization

Light transmittance and color neutrality are critical requirements for an OLED substrate. One issue with the multilayer approach to a UHB is that the separate organic and inorganic layers typically have different indices of refraction. This leads to multiple reflections and usually additional loss of optical transmission through the multilayer stack. One way around this is to engineer the thickness of the layers to create an interference effect that improves light transmission. Unfortunately, the optimal thicknesses for optical performance are usually not the optimal thicknesses for barrier performance and so overall coating optimization involves an undesirable tradeoff [20], [35].

The single-graded-layer UHB approach can circumvent this tradeoff. In particular, since PECVD is utilized to deposit both inorganic and organic materials, there is a large freedom to tailor film properties such as refractive index through film composition. Thus, it is possible to develop a process that yields the same refractive index for both the organic and inorganic materials and hence avoid multiple reflections. We

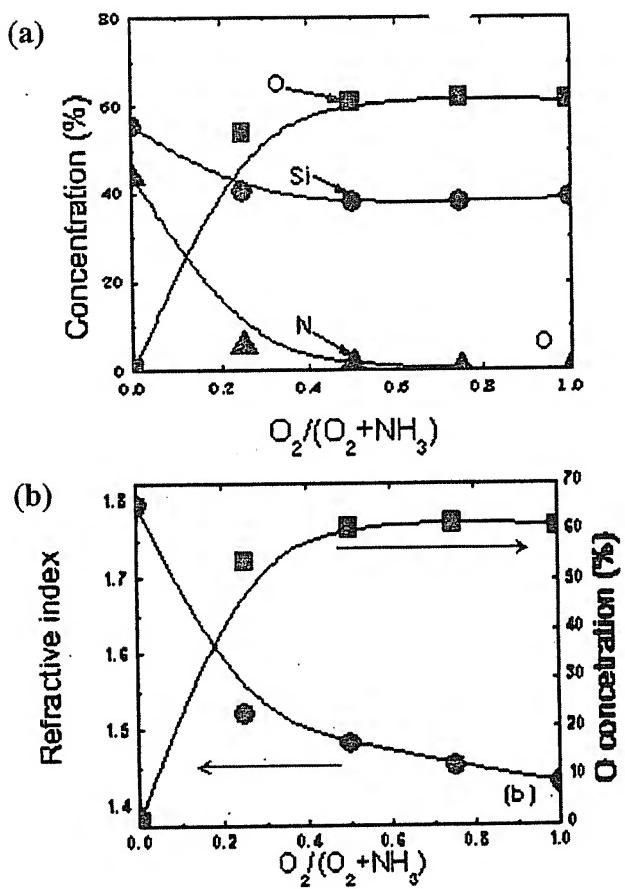


Fig. 9. (a) Coating composition and (b) refractive index at 550 nm for inorganic material as functions of oxygen flow rate.

chose to do this by modifying the inorganic material such that its index matched that of the organic material ( $n \sim 1.5$ ).

Fig. 9 shows the coating composition and refractive index of the inorganic material at 550 nm as a function of oxygen flow rate. The inorganic coatings were deposited on a Si chip at various oxygen flow rates while the total flow rate was maintained at a constant value. The coating composition was obtained using XPS and the refractive index was obtained using spectroscopic ellipsometry. One can see that the atomic oxygen concentration increases rapidly with a small addition of oxygen in the precursor gases, and simultaneously the refractive index dramatically decreases from  $\sim 1.8$  of silicon nitride to  $\sim 1.5$  of silicon oxynitride. Then, the atomic oxygen concentration increases slowly and finally saturates with further increase in oxygen flow rate, and simultaneously the refractive index decreases slowly to  $\sim 1.4$  of silicon oxide.

In order to test the overall optical effect of these inorganic process modifications, graded UHB coatings were deposited onto the polycarbonate films with varying oxygen flow rates for the inorganic process and then the overall light transmittance (%T) through the coated films was collected using a UV-VIS spectrometer. The average %T and the standard deviation of %T were calculated over the wavelength range of 400–700 nm to assess the optical transparency and the amplitude of any interference effects, respectively. Fig. 10 shows these parameters as a function of oxygen flow rate.

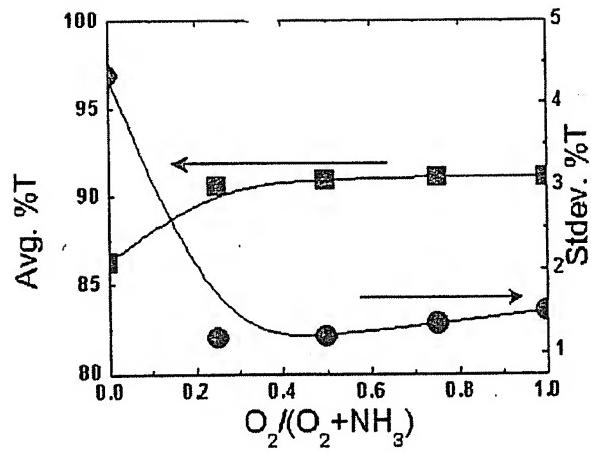


Fig. 10. Average optical transmittance in visible light range and its standard deviation of graded UHB coating as functions of oxygen flow rate used in inorganic coating process.

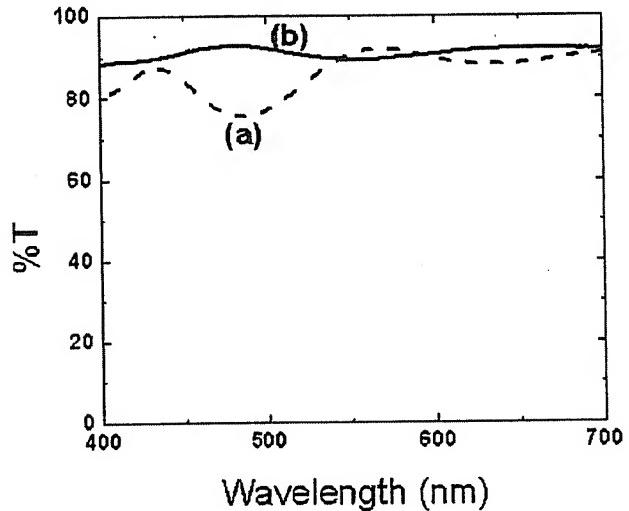


Fig. 11. Optical transmittance spectrum (a) before and (b) after refractive index matching within graded UHB coating.

Note that the average %T is  $\sim 86\%$  when the UHB coating includes silicon nitride as an inorganic material, but it increases to above 90% as the oxygen flow rate in the inorganic process increases. One can also see that the amplitude of interference is at a minimum when the oxygen flow fraction is  $\sim 0.2$ —presumably where the refractive index of the inorganic material matches that of the organic material. Fig. 11 compares the complete %T spectra through two distinct graded UHB coatings: (a) silicon nitride as the base inorganic material (oxygen flow fraction of 0), and (b) silicon oxynitride as the base inorganic material (oxygen flow fraction of 0.25). One can see that with the given silicon oxynitride as the base inorganic material, the single-layer graded barrier coating on the polycarbonate substrate indeed has higher overall transmission and greatly minimized interference fringes relative to that with silicon nitride as the base inorganic material. This demonstrates that highly transparent and essentially color-neutral barrier coatings can be made with our single-layer graded approach to a UHB.

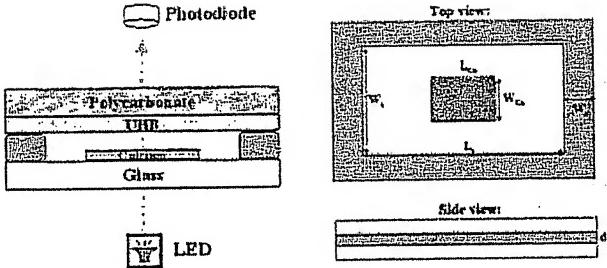


Fig. 12. Illustration of the calcium corrosion test setup and the test cell geometry.

### C. UHB Performance

One major obstacle in the development of a barrier enhanced plastic substrate is the lack of a readily available measurement system for water vapor transmission rate in the  $10^{-5}$ – $10^{-6}$  g/m<sup>2</sup>/day range. Thus, custom-built measuring systems based on the reaction of calcium with water are typically used to assess the hermeticity of UHB coatings [40], [41]. The schematic of a calcium cell, the measurement system, and the cell geometry utilized for our tests is shown in Fig. 12. Calcium is evaporated onto a glass slide and then the test substrate is attached to the slide to cover the exposed calcium. The attachment is made with a perimeter seal outside of the calcium region. As the water vapor permeates through the substrate and/or the edge perimeter seal, or is being released from any internal sources (e.g., residual moisture in adhesive), it reacts with calcium inside the cell and the calcium layer becomes thinner and more transparent as a function of time. Since the optical density (OD) of a film is proportional to its thickness, we can then calculate the WVTR via the following equation:

$$\text{WVTR} = -2A \frac{M[\text{H}_2\text{O}]}{M[\text{Ca}]} \rho_{\text{Ca}} \frac{L_{\text{Ca}} \cdot W_{\text{Ca}}}{L_s \cdot W_s} \frac{d(\text{OD})}{dt} \quad (1)$$

where  $A$  is the scaling factor between calcium thickness and OD,  $M[\text{H}_2\text{O}]$ , and  $M[\text{Ca}]$  are the molar masses of water and Ca with values of 18 and 40.1 amu, respectively,  $\rho_{\text{Ca}}$  is the density of calcium,  $L_{\text{Ca}}$  and  $W_{\text{Ca}}$  are the length and width of the deposited Ca,  $L_s$  and  $W_s$  are the length and width of the permeation area defined by the interior boundary of the edge perimeter seal (Fig. 12), and  $d(\text{OD})/dt$  is the slope of the measured optical absorbance versus time. Details of this testing method are described elsewhere [39].

Several graded UHB samples and reference cells with a glass test sample rather than a UHB-coated plastic sample were prepared and tested with this method at 23 °C and 50% relative humidity (RH). Fig. 13 shows the OD versus time plots for a representative graded UHB and glass/glass reference sample. From these data, WVTR values of  $1.7(\pm 0.5) \times 10^{-5}$  g/m<sup>2</sup>/day for the UHB and  $6.8(\pm 0.1) \times 10^{-6}$  g/m<sup>2</sup>/day for the glass/glass reference cell were calculated using (1). To date, the various graded UHB coatings made in our laboratory span a range from  $5 \times 10^{-6}$  to  $5 \times 10^{-5}$  g/m<sup>2</sup>/day with glass/glass reference cells reading from  $1 \times 10^{-6}$  to  $1 \times 10^{-5}$  g/m<sup>2</sup>/day under

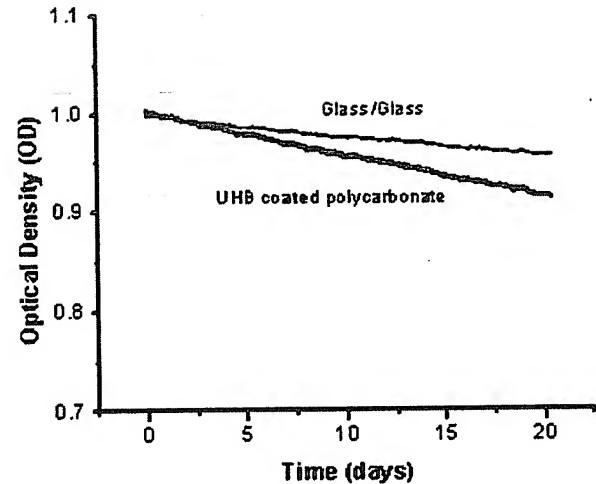


Fig. 13. Optical density versus time plots for UHB and glass/glass reference cells, obtained from the calcium corrosion test.

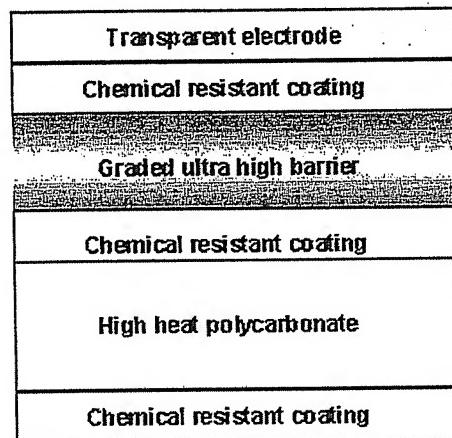


Fig. 14. High heat polycarbonate film with transparent coating package that meets the stringent requirements for application in flexible organic electronics.

these test condition. This is within the range of interest for OLED applications.

### IV. COMPLETE SUBSTRATE PACKAGE

In order to demonstrate a complete substrate package for organic electronic device fabrication, all the components described above—the polycarbonate film, the chemical resistance layers, and the single-layer UHB coating—were integrated together. In addition, a layer of indium-tin-oxide was sputtered onto the top of the substrate as this is the typical starting point for OLED manufacturers. Fig. 14 schematically depicts the integrated package. After fabrication of this total package, a full battery of tests including Ca corrosion tests for WVTR, four-point probe measurements for the ITO sheet resistance, UV-VIS analysis for the optical transparency, the ASTM3359 method for adhesion, TMA for dimensional stability, optical profilometry for the surface roughness, and bend tests for mechanical flexibility were performed. The results of this comprehensive evaluation are summarized in Table 1.

**Table 1**  
Comprehensive Coating Package Performance of GE Plastic  
OLED Substrate

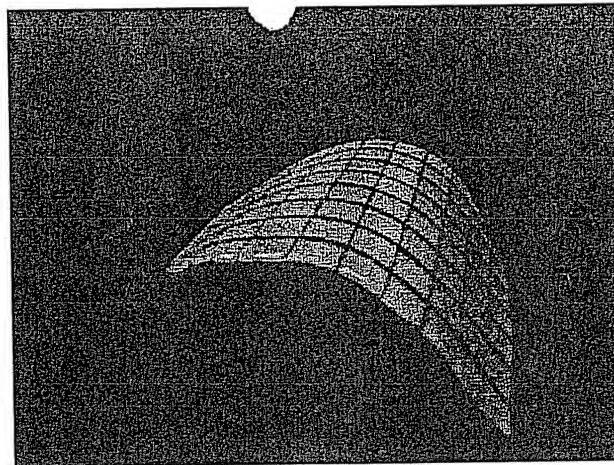
	GE Performance
WVTR	$5 \times 10^{-6} - 5 \times 10^{-5}$ g/m <sup>2</sup> /day
Chemical Resistance	Resistant to commonly used acid, alkali, and solvent
ITO sheet resistance	40 Ω/Sq
Optical Transparency	82 %
Mechanical Flexibility	Bendable around 1" diameter.
Thermo-Mechanical Stability	Sustain 200°C for 1 hr
Adhesion	4B
Thermal dimension stability	Shrinks at 4 ppm/hr at 150°C
Average surface roughness	0.6 nm

The properties depicted in Table 1 are all quite promising for organic electronic device fabrication. However, the final proof of compatibility with OLED processing requires the actual fabrication of a device. Many unanticipated issues such as the presence of particles, handling methods, resistance to a certain set of solvents, stability during high-temperature steps, the effect of mechanical stress due to sealing, performance of the transparent conductor, shelf life, etc. tend to surface during device fabrication. In order to test for these, two-layer polymer OLEDs consisting of PEDOT/PSS [poly(ethylenedioxythiopene)/polysulfonated styrene] as a hole transport layer and a polyfluorene-based light-emitting polymer (LEP) layer were fabricated with our substrate package as the bottom electrode. A series connected architecture described elsewhere [39] was employed to enable a large emitting area. In particular, ten devices consisting of eight series-connected elements, each with area  $1.95 \text{ cm}^2$ , were fabricated on a  $15 \text{ cm} \times 15 \text{ cm}$  substrate. Fabrication was accomplished using the fairly standard procedure described below.

In order to enable device fabrication using conventional batch processing tools, the substrate films were first affixed to 3-mm-wide  $15 \text{ cm} \times 15 \text{ cm}$  square titanium frames by means of double-sided Kapton polyimide tape. The affixed film was cleaned with isopropanol, then a 10-min dwell in an aqueous detergent (Alconox) with ultrasonic agitation, followed by water rinsing and drying.

ITO patterning was accomplished using a photoresist and immersion etching. The photoresist (AZ1512) was applied by means of spin coating and baked for 10 min at  $110^\circ\text{C}$ , producing a film  $1 \mu\text{m}$  thick. The positive photoresist was imaged through a glass mask using a UV collimated light source for 15 s. The image was developed at room temperature for 1 min using OCG 809 (2:1). Following a water rinse and drying, the exposed ITO was removed by immersion for 5 min in a  $45^\circ\text{C}$  solution of 10/10/1 hydrochloric acid/water/nitric acid. The sample was rinsed with water, dried, and the photoresist removed by immersion in acetone. Residual materials were removed by a 10 min dwell in an aqueous detergent (Alconox) with ultrasonic agitation, followed by water rinsing and drying.

The active device layers were deposited by means of spin coating. In particular, an aqueous coating of PEDOT/PSS (Baytron P VP CH 8000 from H.C. Stark) was spin coated and baked at  $110^\circ\text{C}$  to produce a film of 50 nm thickness.



**Fig. 15.** 15-cm square flexible OLED on high heat polycarbonate substrate with graded UHB.

The LEP layer was fabricated using a solution of LUMATION<sup>1</sup> 1304 in xylene. After spincoating and a 10 min bake on a hot plate, a 70-nm-thick LEP layer was produced. A bi-layer cathode made up of NaF and aluminum was then evaporated onto the films through a stainless steel mask. Finally, the devices were encapsulated with a 100-μm-thick foil of aluminum coated with adhesive inside a glove box. The samples were then removed from the glove box for testing.

Fig. 15 provides a picture of the resulting substrate being bent with all devices turned on at a brightness of  $\sim 1000 \text{ cd/m}^2$ . At this brightness, the efficiency, as measured in an integrating sphere, is 8 cd/A. This is comparable to that expected for this LEP material [42]. It thus appears that our polycarbonate/graded UHB substrate package is compatible with a polymer-based OLED fabrication process. Efforts are ongoing to assess the detailed performance characteristics of OLEDs made with this substrate as a function of time and environmental conditions.

## V. CONCLUSION

We have described the development of a transparent plastic substrate technology that provides the high hermeticity that is expected to be required for many organic electronic devices. The key features of this technology are a polycarbonate film with high-temperature capability and a novel single-graded layer UHB coating that can be tuned for refractive index matching. Simple OLEDs were made on this substrate to demonstrate its compatibility with at least one organic electronic device fabrication technology. In order to further develop the technology, efforts need to be placed in optimizing the substrate for all the possible variants of OLED, passive and active matrix backplane, and other organic electronic device fabrication processes. It should be noted that the performance of the underlying plastic film and of the graded UHB coating are not highly coupled to each other and so separate optimization is possible. Thus, if a new transparent polycarbonate or other polymer film with higher temperature capability is developed, it should

<sup>1</sup>LUMATION is a trademark of The Dow Chemical Company.

be possible to apply the graded UHL coating concept with minimal adjustment. This increases the possibility that plastic substrate technologies will be developed for even the most demanding organic electronic device applications.

## ACKNOWLEDGMENT

The authors would like to acknowledge W. F. Nealon for help on OLED device fabrication, and J. J. Chera and M. Larsen for help on thin-film characterizations.

## REFERENCES

- [1] S. R. Forrest, "The path to ubiquitous and low-cost organic electronic appliances on plastic," *Nature*, vol. 428, pp. 911–918, Apr. 2004.
- [2] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Lögdlund, and W. R. Salaneck, "Electroluminescence in conjugated polymers," *Nature*, vol. 397, pp. 121–128, Jan. 1999.
- [3] S. R. Forrest, "Active optoelectronics using thin-film organic semiconductors," *IEEE J. Sel. Topics Quantum Electron.*, vol. 6, no. 6, pp. 1072–1083, Nov.–Dec. 2000.
- [4] C. W. Tang, "Two-layer organic photovoltaic cell," *Appl. Phys. Lett.*, vol. 48, pp. 183–185, Jan. 1986.
- [5] G. Yu, J. Gao, J. Hummelen, F. Wudl, and A. J. Heeger, "Polymer photovoltaic cells: Enhanced efficiencies via a network of internal donor-acceptor heterojunctions," *Science*, vol. 270, pp. 1789–1791, Dec. 1995.
- [6] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, and A. B. Holmes, "Efficient photodiodes from interpenetrating polymer networks," *Nature*, vol. 376, pp. 498–500, Aug. 1995.
- [7] A. J. Lovinger and L. J. Rothberg, "Electrically active organic and polymeric materials for thin-film-transistor technologies," *J. Mater. Res.*, vol. 11, p. 1581, Sep. 1996.
- [8] J. A. Rogers, Z. Bao, K. Baldwin, A. Dodabalapur, B. Crone, V. R. Raju, V. Kuck, H. Katz, K. Amundson, J. Ewing, and P. Drzaic, "Paper-like electronic displays: Large area, rubber stamped plastic sheets of electronics and microencapsulated electrophoretic inks," *Proc. Nat. Acad. Sci.*, vol. 98, pp. 4835–4840, 2001.
- [9] E. S. Snow, J. P. Novak, P. M. Campbell, and D. Park, "Random networks of carbon nanotubes as an electronic material," *Appl. Phys. Lett.*, vol. 82, pp. 2145–2147, Mar. 2003.
- [10] X. Duan, C. Niu, V. Sahl, J. Chen, J. W. Parce, S. Empedocles, and J. L. Goldman, "High-performance thin-film transistors using semiconductor nanowires and nanoribbons," *Nature*, vol. 425, pp. 274–278, Sep. 2003.
- [11] D. B. Mitzi, L. L. Kosbar, C. E. Murray, M. Copel, and A. Afzali, "High-mobility ultrathin semiconducting films prepared by spin coating," *Nature*, vol. 428, pp. 299–302, Mar. 2004.
- [12] B. K. Crone, A. Dodabalapur, R. Sarpeshkar, A. Gelperin, H. E. Katz, and Z. Bao, "Organic oscillator and adaptive amplifier circuits for chemical vapor sensing," *J. Appl. Phys.*, vol. 91, pp. 10 140–10 146, Jun. 2002.
- [13] W. Fix, A. Ullmann, J. Ficker, and W. Clemens, "Fast polymer integrated circuits," *Appl. Phys. Lett.*, vol. 81, pp. 1735–1737, Aug. 2002.
- [14] G. Gelinck, H. E. A. Huitema, E. V. Veenendaal, E. Cantatore, L. Schrijnemakers, J. B. P. H. Van Der Putten, T. C. T. Geuns, M. Beenakkers, J. B. Giesbers, B. Huisman, E. J. Meijer, E. M. Benito, F. J. Touwslager, A. W. Marsman, B. J. E. Van Rens, and D. M. De Leeuw, "Flexible active-matrix displays and shift registers based on solution-processed organic transistors," *Nature Mater.*, vol. 3, pp. 106–110, Feb. 2004.
- [15] J. K. Mahon, J. J. Brown, T. X. Zhou, P. E. Burrows, and S. R. Forrest, "Requirements of flexible substrates for organic light emitting devices in flat panel display applications," *Soc. Vacuum Coat.*, vol. 505/856–7188, pp. 456–459, 1999.
- [16] P. E. Burrows, G. L. Graff, M. E. Gross, P. M. Martin, M. Hall, E. Mast, C. Bonham, W. Bennett, L. Michalski, M. Weaver, J. J. Brown, D. Fogarty, and L. S. Sapochak, "Gas permeation and lifetime tests on polymer-based barrier coatings," *Proc. SPIE—Int. Soc. Opt. Eng.*, vol. 4105, pp. 75–83, 2001.
- [17] J. D. Affinito, M. L. Gross, C. A. Coronado, G. L. Graff, E. N. Greenwell, and P. M. Martin, "A new method for fabricating transparent barrier layers," *Thin Solid Films*, vol. 290–291, pp. 63–67, Dec. 1996.
- [18] H. C. Langowski, A. Melzer, and D. Schubert, "Ultra high barrier layers for technical applications," in *45th Annu. Technical Conf. Proc. Society of Vacuum Coaters*, 2002, pp. 471–475.
- [19] M. S. Weaver, L. A. Michalski, K. Rajan, M. A. Rothman, J. A. Silvermail, J. J. Brown, P. E. Burrows, G. L. Graff, M. E. Gross, P. M. Martin, M. Hall, E. Mast, C. Bonham, W. Bennett, and M. Zumhoff, "Organic light-emitting devices with extended operating lifetimes on plastic substrates," *Appl. Phys. Lett.*, vol. 81, no. 16, pp. 2929–2931, Oct. 2002.
- [20] M. Schaepkens, T. W. Kim, A. G. Erlat, M. Yan, K. W. Flanagan, C. M. Heller, and P. McConnelie, "Ultrahigh barrier coating deposition on polycarbonate substrates," *J. Vac. Sci. Technol. A*, vol. 22, no. 4, pp. 1716–1722, Jul. 2004.
- [21] A. Chwang, M. A. Rothman, S. Y. Mao, R. H. Hewitt, M. S. Weaver, J. A. Silvermail, K. Rajan, M. Hack, J. J. Brown, X. Chu, L. Moro, T. Krajewski, and N. Rutherford, "Thin film encapsulated flexible organic electroluminescent displays," *Appl. Phys. Lett.*, vol. 83, no. 3, pp. 413–415, Jul. 2003.
- [22] W. A. MacDonald, "Engineered films for display technologies," *J. Mater. Chem.*, vol. 14, pp. 4–10, 2004.
- [23] H. Chatham, "Oxygen diffusion barrier properties of transparent oxide coatings on polymeric substrates," *Surf. Coat. Technol.*, vol. 78, pp. 1–9, Jan. 1996.
- [24] W. Decker and B. M. Henry, "Basic principals of thin barrier coatings," in *45th Annu. Soc. Vacuum Coaters Technical Conf.*, 2002, p. 492.
- [25] A. S. da Silva Sobrinho, M. Latreche, G. Czeremuszkin, J. E. Klemberg-Sapieha, and M. R. Wertheimer, "Transparent barrier coatings on polyethylene terephthalate by single- and dual-frequency plasma-enhanced chemical vapor deposition," *J. Vac. Sci. Technol. A*, vol. 16, pp. 3190–3198, Nov. 1998.
- [26] A. S. da Silva Sobrinho, G. Czeremuszkin, M. Latreche, and M. R. Wertheimer, "Defect-permeation correlation for ultrathin transparent barrier coatings on polymers," *J. Vac. Sci. Technol. A*, vol. 18, pp. 149–157, 2000.
- [27] A. G. Erlat, R. J. Spontak, R. P. Clarke, T. C. Robinson, P. D. Haaland, Y. Tropsha, N. G. Harvey, and E. A. Vogler, "SiO<sub>x</sub> gas barrier coatings on polymer substrates: Morphology and gas transport considerations," *J. Phys. Chem. B*, vol. 103, pp. 6047–6055, 1999.
- [28] R. M. Barrer, *Diffusion in and Through Solids*. New York: Cambridge Univ. Press, 1941.
- [29] B. E. Deal and A. S. Grove, "General relationship for the thermal oxidation of silicon," *J. Appl. Phys.*, vol. 36, pp. 3770–3778, Dec. 1965.
- [30] E. H. H. Jamieson and A. H. Windle, "Structure and oxygen-barrier properties of metallized polymer film," *J. Mater. Sci.*, vol. 18, pp. 64–80, Jan. 1983.
- [31] Y. G. Tropsha and N. G. Harvey, "Activated rate theory treatment of oxygen and water transport through silicon oxide/poly(ethylene terephthalate) composite barrier structures," *J. Phys. Chem. B*, vol. 101, pp. 2259–2266, 1997.
- [32] A. P. Roberts, B. M. Henry, A. P. Sutton, C. R. M. Grovenor, G. A. D. Briggs, T. Miyamoto, M. Kano, Y. Tsukahara, and M. Yanaka, "Gas permeation in silicon-oxide/polymer (SiO<sub>x</sub>/PET) barrier films: Role of the oxide lattice, nano-defects and macro-defects," *J. Membrane Sci.*, vol. 208, pp. 75–88, Oct. 2002.
- [33] G. Nisato, M. Kuilder, P. Bouting, L. Moro, O. Philips, and N. Rutherford, "Thin-film encapsulation for OLEDs: Evaluation of multilayer barriers using the Ca test," in *Soc. Information Display, 2003 Int. Symp., Dig. Tech. Papers*, vol. XXXIV, p. P-88.
- [34] L. Moro, T. A. Krajewski, N. M. Rutherford, O. Philips, R. J. Visser, M. E. Gross, W. D. Bennett, and G. L. Graff, "Integrated encapsulation of bottom and top emission OLED displays," *Proc. SPIE—Int. Soc. Opt. Eng.*, vol. 5214, pp. 83–93, 2004.
- [35] J. S. Lewis and M. S. Weaver, "Thin-film permeation-barrier technology for flexible organic light-emitting devices," *IEEE J. Sel. Topics Quantum Electron.*, vol. 10, no. 1, pp. 45–57, Jan.–Feb. 2004.
- [36] G. L. Graff, R. E. Williford, and P. E. Burrows, "Mechanisms of vapor permeation through multilayer barrier films: Lag time versus equilibrium permeation," *J. Appl. Phys.*, vol. 96, pp. 1840–1849, Aug. 2004.
- [37] E. H. Nicollian and J. R. Brews, *MOS Physics and Technology*. New York: Wiley, ch. 16.

- [38] A. S. da Silva Sobrinho, N. Schuhler, J. E. Kriemberg-Sapieha, M. R. Wertheimer, M. Andews, and S. C. Gujrathi, "Plasma-deposited silicon oxide and silicon nitride films on poly(ethylene terephthalate): A multitechnique study of the interphase regions," *J. Vac. Sci. Technol. A*, vol. 16, pp. 2021–2030, 1998.
- [39] A. G. Erlat, M. Schaepkens, T. W. Kim, C. M. Heller, M. Yan, and P. McConnelee, "Ultra-high barrier coatings on polymer substrates for flexible optoelectronics: Water vapor transport and measurement systems," in *47th Annu. Technical Conf. Proc. Soc. Vacuum Coaters*, 2004, pp. 654–663.
- [40] G. Nisato, P. C. P. Bouten, P. J. Slinkerveer, W. D. Bennet, G. L. Graff, N. Rutherford, and L. Wiese, *Asia Display/IDW'01 Proc.*, 2001.
- [41] P. O. Nilsson and G. Forsell, "Optical properties of calcium," *Phys. Rev. B, Condens. Matter*, vol. 16, pp. 3352–3358, 1977.
- [42] *LUMATION Green 1300 Series LEP Data Sheets*, The Dow Chemical Company.

**Min Yan** received the B.S. and M.S. degrees in materials science from Shanghai Jiao Tong University, Shanghai, China, in 1995 and 1998, respectively, and the Ph.D. degree in materials science and engineering from Northwestern University, Evanston, IL, in 2002.

He joined General Electric Global Research, Niskayuna, NY, in 2002 and has been working on the development of barrier coated high heat polymeric substrates for OLEDs.

**Tae Won Kim** received the B.S. degree in chemical engineering from Seoul National University, Seoul, Korea, in 1998 and the Ph.D. degree in chemical engineering from University of California, Santa Barbara, in 2002.

He joined General Electric (GE) Global Research Center, Niskayuna, NY, in 2003 and developed ultra-high barrier coatings for flexible OLED substrates. In 2005, he joined GE Advanced Materials, Strongsville, OH, and has been working on materials for thin-film deposition.

**Ahmet Gün Erlat** received the B.S. degree in metallurgical and materials engineering from Middle East Technical University, Ankara, Turkey, in 1996, the M.S. degree in materials science and engineering from North Carolina State University, Raleigh, NC, in 1998, and the Ph.D. degree in materials from the University of Oxford, Oxford, U.K., in 2002.

He joined General Electric Global Research, Niskayuna, NY, in 2003 and has been working on the development of barrier coated high heat polymeric substrates for OLEDs.

**Matthew Pellow** received the B.A. degree in chemistry from Columbia University, New York, in 2003. He is a graduate student in chemistry at Stanford University, Palo Alto, CA.

He joined General Electric Global Research, Niskayuna, NY, in 2003 and worked with encapsulants, barrier film development, and rubber modification.

**Donald F. Foust** received the B.S. degree in chemistry from Bucknell University, Lewisburg, PA, in 1976 and the Ph.D. degree in inorganic chemistry from the University of Massachusetts, Amherst, in 1981.

In 1986 he joined General Electric Global Research, Niskayuna, NY, and has worked in the areas of miniature electronics, environmental chemistry, and metal/polymer adhesion. He is currently leading the development of a roll-to-roll process for plastic-based OLEDs.

**Jie Liu** received the B.S. degree in chemical engineering from Dalian University of Technology, China, in 1993, the M.S. degree in chemistry from the Institute of Chemistry, Chinese Academy of Science, Beijing, China, in 1996, and the Ph.D. degree in material sciences and engineering from the University of California, Los Angeles, in 2001.

In 2002 he joined General Electric Global Research, Niskayuna, NY, and has been working on organic electronic devices

**Marc Schaepkens** received the Ir/M.S. degree in applied physics from Eindhoven University of Technology, Eindhoven, The Netherlands, in 1996 and the Ph.D. degree in physics from the University at Albany, Albany, NY, in 1999.

In 2000 he joined General Electric (GE) Global Research, Niskayuna, NY, and worked on various projects in the area of thin film coatings on polymeric substrates. In 2004 he joined the GE Advanced Materials business as Technology Master Black Belt.

**Christian M. Heller** received the M.S. degree in technical physics from the Technical University Graz, Graz, Austria, in 1992.

He has been working on OLEDs and packaging issues first at the Los Alamos National Laboratory, Los Alamos, NM, then at eMagin Corporation, NY, and since 2001 at General Electric Global Research, Niskayuna, NY.

**Paul A. McConnelee** received the B.S. degree in electrical engineering from Union College in 1978.

He joined General Electric (GE) in 1972, where he has been involved in process development, electronic design, electronic packaging, and cleanroom engineering. He presently is Cleanroom and Engineering Operations leader at GE Global Research, Niskayuna, NY.

**Thomas P. Feist** received the B.A. degree in chemistry from Williams College, Williamstown, MA, in 1985 and the Ph.D. degree in materials science and engineering from the University of Pennsylvania, Philadelphia, in 1991.

In 1996, he joined General Electric (GE) Global Research, Niskayuna, NY, and has been working on various aspects of optical data storage and thin films technology. He is currently manager of the Thin Films Laboratory in the Micro and Nano Structures Technologies organization at GE.

**Anil R. Duggal** received the A.B. degree in chemistry from Princeton University, Princeton, NJ, in 1987 and the Ph.D. degree in physical chemistry from the Massachusetts Institute of Technology, Cambridge, in 1992.

In 1992, he joined General Electric (GE) Global Research, Niskayuna, NY, and has been working on various aspects of optoelectronics. He is currently leading the organic electronics advanced technology program at GE.

# Transparent hybrid inorganic/organic barrier coatings for plastic organic light-emitting diode substrates

Tae Won Kim,<sup>a)</sup> Min Yan, Ahmet Gün Erlat, Paul A. McConnelee, Mathew Pellow, John Deluca, Thomas P. Feist, and Anil R. Duggal  
*General Electric Global Research Center, Schenectady, New York 12309*

Marc Schaeckens  
*General Electric Advanced Materials, Strongsville, Ohio 44149*

(Received 4 January 2005; accepted 14 March 2005; published 27 June 2005)

We have developed a coating technology to reduce the moisture permeation rate through a polycarbonate plastic film substrate to below  $1 \times 10^{-5}$  g/m<sup>2</sup>/day using plasma-enhanced chemical vapor deposition. Unlike other ultrahigh barrier (UHB) coatings comprised of inorganic and organic multilayers, our UHB coating comprises a graded single hybrid layer of inorganic and organic materials. Hardness and modulus of the inorganic and the organic materials are tailored such that they are similar to those of typical glass-like materials and thermoplastics, respectively. In this barrier structure, the composition is periodically modulated between the inorganic and the organic materials, but instead of having distinctive interfaces between two materials, there are "transitional" zones where the coating composition changes continuously from one material to another. Our UHB coating also has superior visible light transmittance and color neutrality suitable for the use of display and lighting device substrates. © 2005 American Vacuum Society.

[DOI: 10.1116/1.1913680]

## I. INTRODUCTION

The use of plastic film substrates enables fabrication of new applications in the area of flexible opto-electronics, such as flexible display and lighting, using low-cost roll-to-roll fabrication technologies. One major limitation of bare plastic film substrates in these applications is the rapid oxygen and moisture diffusion through the substrates and subsequent moisture and oxygen induced degradation of the optoelectronic devices. Thus, it is imperative for the plastic substrate to have hermetic coatings to prevent moisture and oxygen permeation.<sup>1–6</sup> There has accumulated a great amount of literature over the last 20 years on applying vacuum-deposited inorganic layers on plastic substrates in order to improve the barrier properties against water vapor and oxygen permeation.<sup>7–11</sup> Although bulk inorganics such as a perfect SiO<sub>2</sub> film are effectively impermeable to moisture and oxygen,<sup>12,13</sup> single-layer inorganic barrier coatings reduce the moisture and oxygen permeation rates by at most two to three orders of magnitude as compared to those through the uncoated plastic.<sup>9,10,14–16</sup> The reason for the limited barrier improvement attainable with a single inorganic barrier coating is now well understood to be due to nanometer- to micron-sized defects in the coating that originate either from the surface roughness of the underlying substrate or from the inorganic coating processing conditions.<sup>17</sup> These defects provide easy pathways for moisture and oxygen diffusion, and thus limit the barrier performance. Evidence of this defect-driven permeation mechanism can be found through studies of permeation rate as a function of inorganic coating thick-

ness. Permeation rate through a defect-free bulk film should exhibit Fickian diffusion and should thus vary inversely with film thickness. However, this is not normally observed for thin-film barrier coatings. Typically, the gas permeation rate reduces rapidly by two to three orders of magnitude with increasing coating thickness up to a "critical thickness" of 10–30 nm but, for larger thicknesses, the permeation rate does not decrease further.<sup>10,16</sup> Thus, regardless of barrier material or deposition method, the best barrier performance from a single-layer inorganic coating is several orders of magnitude short of the organic light-emitting diode (OLED) requirement.

In order to meet the stringent requirements put forth for the design of OLEDs and other organic electronic devices on plastic substrates, a robust coating design should be realized that avoids the hindrance of barrier improvement by defects. Multilayer barrier structures comprised of multiple sputter-deposited aluminum oxide inorganic layers separated by polymer multilayer (PML) processed organic layers have demonstrated promising moisture permeation rates in the range of  $10^{-6}$ – $10^{-5}$  g/m<sup>2</sup>/day.<sup>18–20</sup> It is commonly understood that organic layers decouple the defects in the inorganic layers and thus prevent their propagation from one inorganic layer to the other.<sup>21</sup> A modeling study suggests that this defect decoupling due to the organic/inorganic multilayers forces a tortuous path for moisture and oxygen diffusion, and thus reduces the permeation rate by several orders of magnitude.<sup>16</sup> Another study suggests that the inorganic/organic multilayer stack leads to higher performance through a transient rather than steady-state phenomenon.<sup>22</sup> Regardless of mechanism, this multilayer barrier stack approach appears to be capable of yielding the required level of performance for OLED applications.

<sup>a)</sup>Current address: General Electric Advanced Materials, Strongsville OH 44149; electronic mail: taewon.kim@ge.com

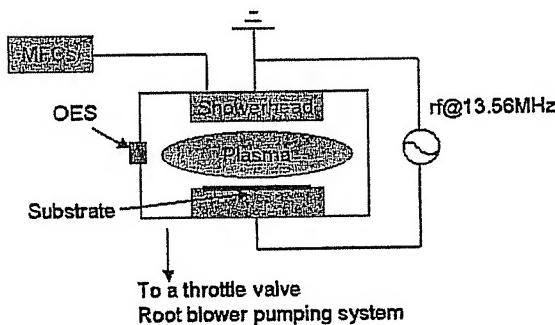


FIG. 1. The schematic of the plasma reactor.

One potential limitation of the multilayer stack approach is that this type of structure tends to suffer from poor adhesion and delamination, especially during the thermal cycles of the OLED fabrication processes, since the inorganic and organic layers have sharp interfaces with weak bonding structure due to the nature of the sputter deposition and PML processes.<sup>23,24</sup> In order to overcome this, we have developed a graded ultrahigh barrier (UHB) coating using plasma-enhanced chemical vapor deposition (PECVD) that can effectively stop defects from propagating through the coating thickness. In this article, we describe the fabrication of the UHB coating in a parallel plate capacitively coupled plasma reactor and its properties, including barrier performance and optical transparency.

## II. EXPERIMENTS

### A. PECVD reactor

The experiments were conducted in a commercially available parallel plate capacitively coupled plasma reactor (Plasmatherm 790) shown schematically in Fig. 1.<sup>16</sup> This type of reactor is commonly used to etch polysilicon or deposit thin films. This reactor is equipped with optical emission spectrometer (Ocean Optics USB2000) to monitor the optical emissions from the plasma during the process. Radio frequency power in the range of 100–500 W at 13.56 MHz is capacitively coupled to plasma through a bottom electrode. The electrode and reactor walls were kept constant at 55 °C by a cooling system. Gas flow into the reactor is controlled by mass flow controllers (MFCs). The gases enter the reactor through the showerhead 1 in. above the bottom electrode, and are pumped by a 270 m<sup>3</sup>/h root blower pump package. The reactor base pressure is below 10 mTorr and typical operating pressure is between 100 and 1000 mTorr. The reactor pressure is controlled by a variable position butterfly valve. The 125 μm thick high heat polycarbonate films were cut

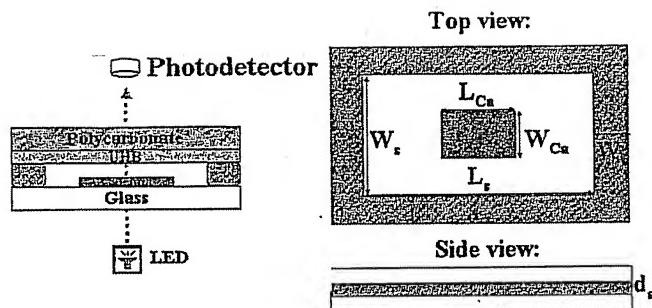
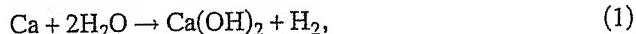


FIG. 2. Illustration of the calcium corrosion test setup and the test cell geometry.

into pieces, each 200 mm in diameter, which were framed between two aluminum rings for the ease of handling, and placed on the bottom electrode.

### B. Ca corrosion test

One major obstacle in developing the UHB coatings is the lack of a readily available measurement system for the water vapor transmission rate (WVTR) in the range of 10<sup>-5</sup>–10<sup>-6</sup> g/m<sup>2</sup>/day. In this study, a WVTR measurement system was built based principally on the degradation of Ca as it reacts with water vapor.<sup>25,26</sup> The schematics of a calcium cell, the measurement system, and the cell geometry are shown in Fig. 2. As water vapor and oxygen permeate through the substrate and/or the edge perimeter seal, or are being released from any internal sources (e.g., residual moisture in adhesive), they react with calcium inside the cell according to the following reactions:<sup>26,27</sup>



It has been shown in a similar technique that oxidation would account for less than 5% of the calcium degradation.<sup>26</sup> Therefore, reaction (1) is predominant. As water vapor permeation progresses, the calcium layer becomes thinner and more transparent. Since the optical density (OD) of a film is proportional to its thickness, WVTR can be calculated using

$$\text{WVTR} = -2A \frac{M[\text{H}_2\text{O}]}{M[\text{Ca}]} \rho_{\text{Ca}} \frac{L_{\text{Ca}} W_{\text{Ca}}}{L_s W_s} \frac{d(\text{OD})}{dt}, \quad (3)$$

where  $A$  is the scaling factor between calcium thickness and OD,  $M[\text{H}_2\text{O}]$  and  $M[\text{Ca}]$  are the molar masses of water and Ca with values of 18 and 40.1 amu, respectively;  $\rho_{\text{Ca}}$  is the density of calcium;  $L_{\text{Ca}}$  and  $W_{\text{Ca}}$  are the length and width, respectively, of the deposited Ca;  $L_s$  and  $W_s$  are the respec-

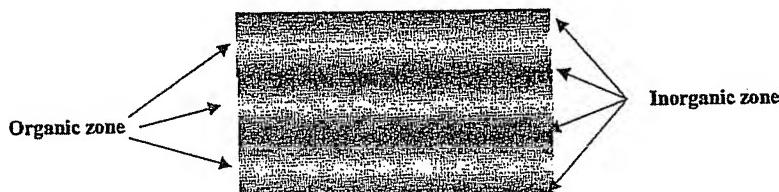


FIG. 3. The schematic of the graded inorganic/organic UHB coating.

TABLE I. Conditions of two base PECVD processes and material properties.

	Inorganic process	Organic process
Precursors	$\text{SiH}_4$ (2% in He) $\text{NH}_3$ $\text{O}_2$	$\text{SiC}_x\text{H}_y$ (C weight % >50%) Ar
Flow rate (sccm)	20–500	50–100
Pressure (mTorr)	100–1000	100–1000
rf power (W)	100–400	100–400
Film hardness (GPa)	10–15	<1
Film modulus (GPa)	100–500	<10
Film %T	>95%	>95%
Deposition rate (nm/min)	40–60	40–80

tive length and width of the permeation area defined by the interior boundary of the edge perimeter seal (Fig. 2), and  $d(\text{OD})/dt$  is the slope of the measured optical absorbance as a function of time. More details of the calcium test cell fabrication and testing procedures have been described elsewhere.<sup>28</sup>

### III. RESULTS AND DISCUSSION

The UHB coating consists of a graded single hybrid layer made up of inorganic and organic materials as schematically shown in Fig. 3. In this barrier structure, the organic materials effectively decouple defects growing in the normal direction to the film but, instead of having a sharp interface between inorganic and organic materials, there are “transitional” zones where the coating composition varies continuously from inorganic to organic and vice versa. These “transitional” zones bridge inorganic and organic materials, resulting in a single layer structure with improved mechanical stability and stress relaxation,<sup>21</sup> relative to that of multilayer barrier structures.

#### A. Fabrication of graded UHB coating

There are two base PECVD processes required to fabricate the UHB coating: an inorganic and an organic process. The inorganic process utilizes a combination of silane (2%

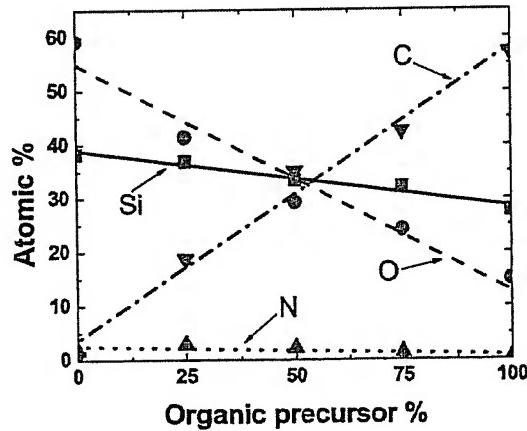


FIG. 4. XPS analyses on the coating composition as a function of precursor gas composition.

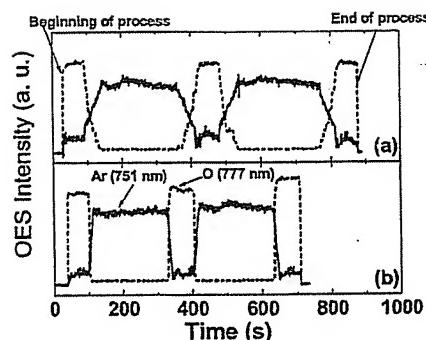


FIG. 5. Time-resolved optical emission spectra for the PECVD graded UHB processes with (a) 40 nm and (b) 5 nm of the “transitional” zone thickness.

silane diluted in He), ammonia, and oxygen gases to create a material composition ranging between silicon nitride and silicon oxide. The organic process includes a combination of organosilicon precursor and Ar gases to create a Si-containing organic material. The inorganic and the organic processes were tailored such that the resulting materials have similar hardness and elastic modulus to those of glass-like materials and thermoplastics, respectively. Table I summarizes the process conditions and material properties. Hereafter, the inorganic and the organic materials are defined as those deposited with 0% and 100% organic precursor concentration, respectively. The composition of the inorganic material (0% organic precursor) and the organic one (100% organic precursor) can be found in Fig. 4.

Although PECVD inorganic film, such as silicon oxide and aluminum oxide, deposited on organic materials by nature has tens of nanometers thick “transitional” regions that exhibit a continuously graded composition between inorganic and organic materials due to ion bombardment,<sup>21</sup> high energy ion bombardment normally results in a highly stressed film, which adversely affects the adhesion of subsequent layers. For instance, OLED devices typically require the deposition of a transparent conductive oxide electrode such as indium tin oxide on top of the UHB. A low stress

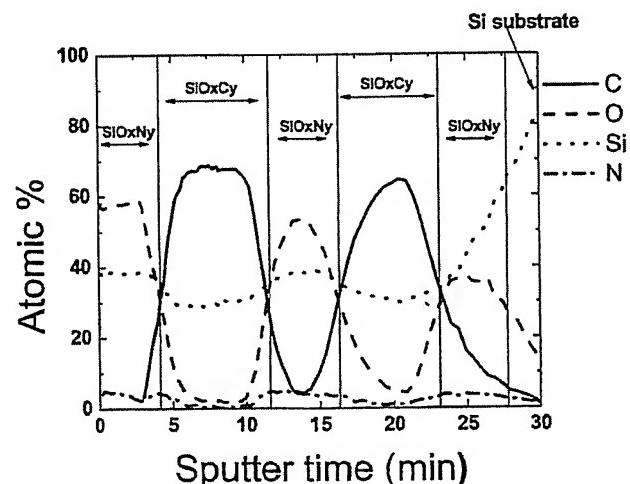


FIG. 6. Depth-profile XPS spectrum for the graded inorganic/organic UHB coating.

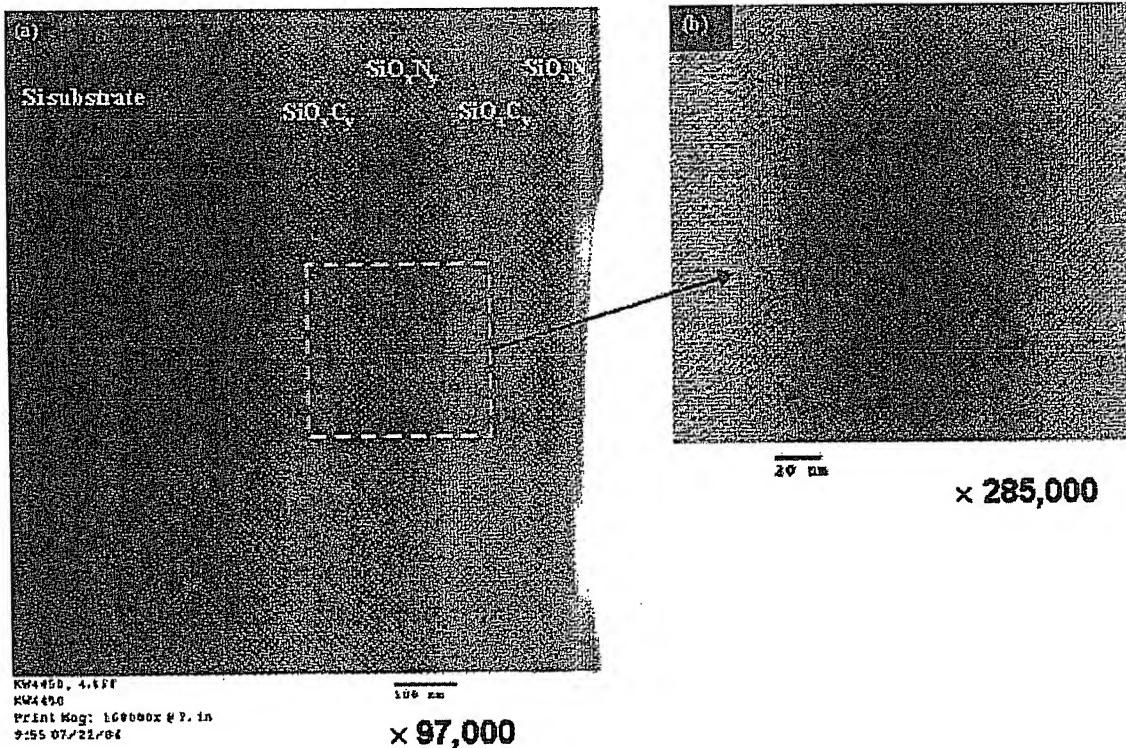


FIG. 7. Cross-sectional TEM images of the graded UHB coating with (a) low magnification and (b) high magnification.

barrier coating is desirable for better adhesion of this layer. Thus, instead of resorting to high ion bombardment energy, our graded UHB structure is obtained by gradually mixing the inorganic and the organic processes. At constant pressure and rf power, each mass flow controller for individual process gases is programmed to achieve continuous compositional changes, while the plasma remains on, in order to achieve a gradual change in the coating composition from inorganic to organic materials and vice versa. For example, if one wants to achieve a coating composition that comprises 90% inorganic and 10% organic materials, MFC values for the inorganic and the organic process gases are set at 90% and 10% with respect to their original values, respectively. The thickness of the "transitional" zone is determined by the time to change the precursor gas composition from the inorganic process to the organic one and vice versa. Typically, due to the nonlinearity of the plasma process, mixing of precursors for two different processes often results in unexpected coating compositions unless the process conditions are carefully selected. In order to prevent this possibility, the inorganic and the organic processes were developed at the same pressure and rf power. In addition, the inorganic and the organic processes were optimized to have comparable deposition rates.

In order to ensure that coatings with mixed organic and inorganic compositions could be deposited by keeping all PECVD process variables constant and by changing only the gas composition, coatings deposited from selected gas combinations were analyzed. Figure 4 shows the results of x-ray photoelectron spectroscopy (XPS) analysis of these coatings. For these measurements, the coatings were deposited onto a

silicon substrate and a few monolayers of the coating were removed from the top surface by low energy Ar sputtering to eliminate surface contamination. Figure 4 indicates that a linear change in the coating composition can be achieved with a linear change in the precursor gas composition. For example, the carbon concentration is nearly zero when the precursor gas composition is that of the pure inorganic process, and increases linearly with increasing percentage of the organic precursor. Note that the precursor gases for the organic process do not contain oxygen; the oxygen present in the 100% organic process is due to desorption from the reactor and/or oxidation of the organic coating at the atmosphere.

Based on these results, processes were developed to create a single coating with the graded structure depicted in Fig. 3 and varying thickness of the "transitional" zones between inorganic and organic materials. Figures 5(a) and 5(b) compare the time-resolved optical emission spectra obtained during processing for two different processes with planned "transitional" zones of 40 and 5 nm, respectively. For these measurements, representative emission lines ( $\text{O}$  at 777 nm for the inorganic process and  $\text{Ar}$  at 751 nm for the organic process) were selected to monitor the precursor composition change during the UHB deposition. The plasma was on for the whole time at constant pressure and rf power during the process. Figure 5 clearly indicates that a continuous change in the plasma composition is achieved during both UHB processes. The  $\text{O}$  emission intensity that represents the inorganic precursor fraction is high during the inorganic process, and decreases continuously towards a baseline when the fraction of the organic process gases monotonically increases during

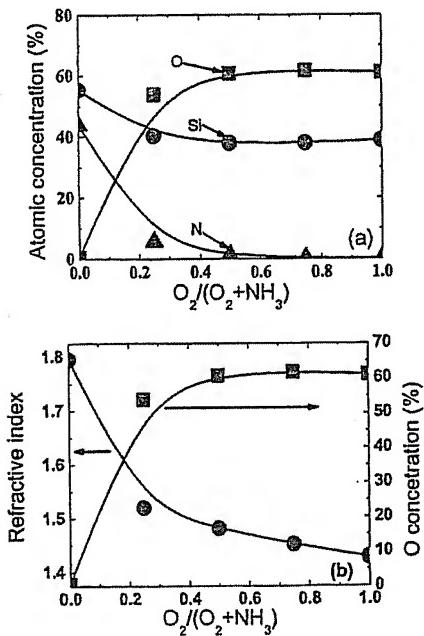


FIG. 8. (a) Coating composition and (b) the refractive index at 550 nm of the inorganic material as a function of oxygen flow rate.

the “transitional” zone process. At the same time, the Ar emission intensity that represents the organic precursor fraction increases continuously.

In order to verify that the desired graded composition coatings were made, depth-profile XPS measurements and cross-sectional transmission electron microscopy (TEM) were performed on the final coatings. The depth-profile XPS analysis for the 40 nm transition zone sample shown in Fig. 5(a) is shown in Fig. 6. The data clearly suggest a continuous change in composition as a function of sputter time and hence depth. The XPS depth profiling was accomplished with low energy Ar sputtering. However, there is still the possibility that the apparently continuous change in composition observed may be an artifact caused by chemical changes of the surface induced by mixing or preferential sputtering of the elements.<sup>23</sup> In order to eliminate this interpretation, cross-sectional TEM analysis was performed in

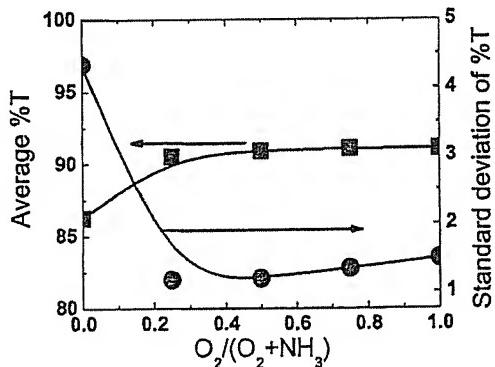


FIG. 9. The overall visible light transmittance and its standard deviation of the graded UHB coating as a function of oxygen flow rate in the inorganic process.

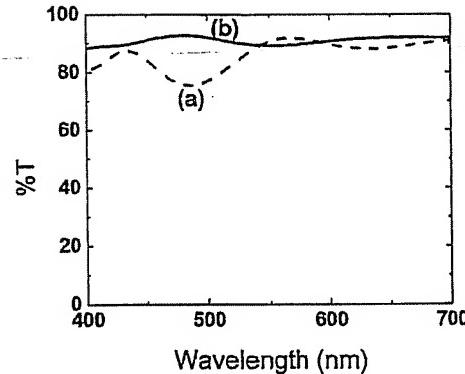


FIG. 10. The complete %T spectra through two distinctive UHB coatings: (a) silicon nitride as the base inorganic material (oxygen flow fraction of 0), and (b) silicon oxynitride as the base inorganic material (oxygen flow fraction of 0.25).

parallel on the same coating. Figure 7 shows representative TEM images. The images clearly depict a graded structure without a discrete interface.

### B. Refractive index matched UHB

Superior light transmittance and color neutrality is another critical substrate requirement for optoelectronic devices such as OLEDs. One issue with the multilayer approach to a UHB is that the separate organic and inorganic layers typically have different indices of refraction. This leads to multiple reflections and usually additional loss of optical transmission through the multilayer stack. One way around this is to engineer the thickness of the layers to create an interference effect that improves light transmission. Unfortunately, the optimal thicknesses for optical performance are usually not the optimal thicknesses for barrier performance, so that overall coating optimization involves an undesirable tradeoff.<sup>16,21</sup>

The single graded layer UHB approach can circumvent this tradeoff. In particular, since PECVD is utilized to deposit both inorganic and organic materials, there is a large freedom to tailor film properties such as refractive index through film composition. Thus, it is possible to develop a process that yields the same refractive index for both the organic and inorganic materials and hence avoid multiple reflections. We chose to do this by modifying the inorganic material such that its index matched that of the organic one ( $n \sim 1.5$ ).

Figures 8(a) and 8(b) show the coating composition and refractive index of the inorganic material at 550 nm as a function of oxygen flow rate. The inorganic coatings were deposited on a Si chip at various oxygen flow rates while total flow rate was maintained at a constant value. The coating composition was obtained using XPS and the refractive index was obtained using spectroscopic ellipsometry. One can see that the atomic oxygen concentration increases rapidly with a small addition of oxygen in the precursor gases, and simultaneously refractive index dramatically decreases from  $\sim 1.8$  (silicon nitride) to  $\sim 1.5$  (silicon oxynitride). Atomic oxygen concentration then increases slowly and

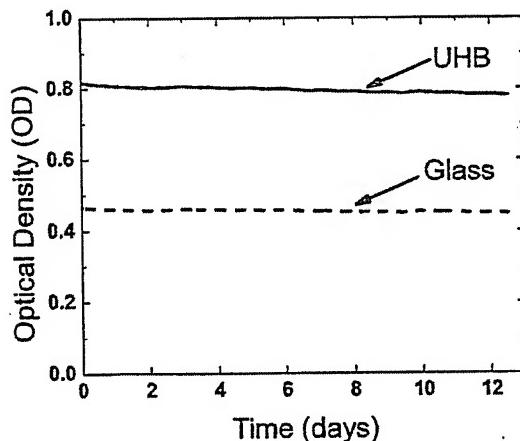


FIG. 11. Optical density vs time plots for the UHB and glass/glass reference cells, obtained from the calcium corrosion test.

finally saturates with a further increase in oxygen flow rate, and refractive index decreases slowly to  $\sim 1.4$  (silicon oxide).

In order to test the overall effect of these inorganic process changes, the UHB coatings were deposited onto the polycarbonate films with the various oxygen flow rates for the inorganic process and the overall light transmittance ( $\%T$ ) through the coated films was collected using a UV-Vis spectrometer. An average  $\%T$  and its standard deviation were calculated over the wavelength range of 400–700 nm to assess the optical transparency and the amplitude of any interference effects, respectively. Figure 9 shows these parameters as a function of oxygen flow rate. Note that the average  $\%T$  is  $\sim 86\%$  when the UHB coating includes silicon nitride as an inorganic material, but it increases to above 90% as the oxygen flow rate in the inorganic process increases. One can also see that the amplitude of interference is at a minimum when the oxygen flow fraction is  $\sim 0.2$ , where the refractive index of the inorganic material matches that of the organic material. Figure 10 compares the complete  $\%T$  spectra through two distinctive UHB coatings: (a) silicon nitride as the base inorganic material (oxygen flow fraction of 0), and (b) silicon oxynitride as the base inorganic material (oxygen flow fraction of 0.25). One can see that with the given silicon oxynitride as the inorganic material, the single layer graded barrier coating on the polycarbonate substrate indeed has higher overall transmission and greatly minimized interference fringes relative to that with silicon nitride as the base inorganic material. This demonstrates that highly transmissive and essentially color neutral barrier coatings can be made with our single layer graded approach to an UHB.

### C. Ultrahigh barrier performance

The graded UHB coating with planned 40 nm thick “transitional” zones shown in Fig. 5(a) was fabricated on the polycarbonate substrate, and the test cells along with glass/glass reference cells were prepared as depicted in Fig. 3. The Ca corrosion test was performed at 25 °C and 50% relative humidity. Figure 11 shows selected OD changes through (a)

the UHB and (b) the glass/glass reference cells as a function of time, from which WVTR values of  $8.6 (\pm 0.3) \times 10^{-6} \text{ g/m}^2/\text{day}$  for the UHB and  $5.9 (\pm 0.5) \times 10^{-6} \text{ g/m}^2/\text{day}$  for the glass/glass reference cell were calculated using Eq. (3). Note that since glass is effectively a perfect barrier, WVTR of the glass/glass reference cell represents the moisture permeation through the edge perimeter seals.

### IV. SUMMARY AND CONCLUSIONS

We have developed an ultrahigh barrier coating of a graded single hybrid layer made up of inorganic and organic materials using PECVD. In this barrier structure, the composition of the coating modulates periodically between the inorganic and the organic materials. The organic material effectively prevents the propagation of the defects in the coating, and thus improves the barrier performance by several orders of magnitude as compared to that of a single layer inorganic coating. In this barrier structure, however, instead of having a distinctive interface between inorganic and organic materials, there are “transitional” zones where the coating composition varies continuously from inorganic to organic and vice versa. These “transitional” zones bridge inorganic and organic materials resulting in a single-layer structure. In addition, the refractive index of the inorganic material was engineered to match that of the organic material that one can avoid multiple reflections and thus obtain superior visible light transmittance. The moisture permeation rate of the polycarbonate substrate with the UHB coating measured by the Ca corrosion test is less than  $1 \times 10^{-5} \text{ g/m}^2/\text{day}$ , meeting the stringent OLED substrate requirements.

### ACKNOWLEDGMENTS

This work was supported in part by the USDC/ARL program (Grant MDA972-93-2-0014). The authors would like to thank John J. Chera and Michael Larsen for the thin film characterizations.

- <sup>1</sup>A. R. Duggal, J. J. Shiang, C. M. Heller, and D. F. Foust, *Appl. Phys. Lett.* **80**, 3470 (2002).
- <sup>2</sup>A. R. Duggal, D. F. Foust, W. F. Nealon, and C. M. Heller, *Appl. Phys. Lett.* **82**, 2580 (2003).
- <sup>3</sup>J. K. Mahon, J. J. Brown, T. X. Zhou, P. E. Burrows, and S. R. Forrest, 42nd Ann. Tech. Conf. Proceedings (Society of Vacuum Coaters), 1999, p. 456.
- <sup>4</sup>M. S. Weaver *et al.*, *Appl. Phys. Lett.* **81**, 2929 (2002).
- <sup>5</sup>A. Chwang *et al.*, *Appl. Phys. Lett.* **83**, 413 (2003).
- <sup>6</sup>G. Nisato and Y. Leterrier, *Mater. Res. Soc. Symp. Proc.* **769**, H1.4 (2003).
- <sup>7</sup>H. Chatham, *Surf. Coat. Technol.* **78**, 1 (1996).
- <sup>8</sup>W. Decker and B. M. Henry, 45th Ann. Tech. Conf. Proceedings (Society of Vacuum Coaters), 2002, p. 492.
- <sup>9</sup>A. S. da Silva Sobrinho, M. Latreche, G. Czeremuszkin, J. E. Klemburg-Sapieha, and M. R. Wertheimer, *J. Vac. Sci. Technol. A* **16**, 3190 (1998).
- <sup>10</sup>A. S. da Silva Sobrinho, G. Czeremuszkin, M. Latreche, and M. R. Wertheimer, *J. Vac. Sci. Technol. A* **18**, 149 (2000).
- <sup>11</sup>A. G. Erlat, R. J. Spontak, R. P. Clarke, T. C. Robinson, P. D. Haaland, Y. Tropsha, N. G. Harvey, and E. A. Vogler, *J. Phys. Chem. B* **103**, 6047 (1999).
- <sup>12</sup>R. M. Barrer, *Diffusion In and Through Solids* (Cambridge University

- Press, New York, 1941).
- <sup>13</sup>B. E. Deal and A. S. Grove, *J. Appl. Phys.* **36**, 3770 (1965).
- <sup>14</sup>E. H. H. Jamieson and A. H. Windle, *J. Mater. Sci.* **18**, 64 (1983).
- <sup>15</sup>Y. G. Tropsha and N. G. Harvey, *J. Phys. Chem. B* **101**, 2259 (1997).
- <sup>16</sup>M. Schaepkens, T. W. Kim, A. G. Erlat, M. Yan, C. M. Flanagan, C. M. Heller, and P. A. McConnelee, *J. Vac. Sci. Technol. A* **22**, 1716 (2004).
- <sup>17</sup>A. P. Roberts, B. M. Henry, A. P. Sutton, C. R. M. Grovenor, G. A. D. Briggs, T. Miyamoto, M. Kano, Y. Tsukahara, and M. Yanaka, *J. Membr. Sci.* **208**, 75 (2002).
- <sup>18</sup>M. S. Weaver *et al.*, *Appl. Phys. Lett.* **81**, 2929 (2002).
- <sup>19</sup>G. Nisato, M. Kuilder, P. Bouten, L. Moro, O. Philips, and N. Rutherford, Society for Information Display, 2003 International Symposium, Digest of Technical Papers, 2003, Vol. XXXIV, p. 88.
- <sup>20</sup>L. Moro, T. A. Krajewski, N. M. Rutherford, O. Philips, R. J. Visser, M. E. Gross, W. D. Bennett, and G. L. Graff, *Proc. SPIE* **5214**, 83 (2004).
- <sup>21</sup>J. S. Lewis and M. S. Weaver, *IEEE J. Sel. Top. Quantum Electron.* **10**, 45 (2004).
- <sup>22</sup>G. L. Graff, R. E. Williford, and P. E. Burrows, *J. Appl. Phys.* **96**, 1840 (2004).
- <sup>23</sup>E. H. Nicollian and J. R. Brews, *MOS Physics and Technology* (Wiley, New York) Chap. 16.
- <sup>24</sup>A. S. da Silva Sobrinho, N. Schuhler, J. E. Klemborg-Sapieha, M. R. Wertheimer, M. Andrews, and S. C. Gujrathi, *J. Vac. Sci. Technol. A* **16**, 2021 (1998).
- <sup>25</sup>G. Nisato, P. C. P. Bouten, P. J. Slinkerveer, W. D. Bennet, G. L. Graff, N. Rutherford, and L. Wiese, *Asia Display/IDW Proc.*, 2001.
- <sup>26</sup>P. O. Nilsson and G. Forsell, *Phys. Rev. B* **16**, 3352 (1977).
- <sup>27</sup>R. Paetzold, A. Winnacker, D. Henseler, V. Cesari, and K. Heuser, *Rev. Sci. Instrum.* **74**, 5147 (2003).
- <sup>28</sup>A. G. Erlat, M. Schaepkens, T. W. Kim, C. M. Heller, M. Yan, and P. McConnelee, 47th Ann. Tech. Conf. Proceedings (Society of Vacuum Coaters), 2004 (in press).

**XI. Related Proceedings Appendix.**

**A. None.**